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Transactions of the Faraday Society

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS

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VOL. VIII. OCTOBER, 1912. PARTS 1 AND 2.

DRY BATTERIES: THE RELATION BETWEEN THE INCIDENCE OF THE DISCHARGE AND THE RELATIVE CAPACITY OF CELLS OF DIFFERENT MANUFACTURE.

By S. W. MELSOM, A.M.I.E.E. (from the National Physical Laboratory).

(*A Paper read before the Faraday Society, Tuesday, March* 26, 1912, MR. ALEXANDER SIEMENS, M.INST.C.E., VICE-PRESIDENT, *in the Chair.*)

This paper gives the results of an investigation which was made in order to ascertain to what extent the tests in general use afford an indication of the relative merits of dry cells of different manufacture.

The tests in general use, or those specified by the various large users, vary largely as regards the incidence of the discharge; in fact, practically speaking, no two of the large users of cells were agreed as to the method of testing likely to give the best comparative results. It was therefore felt desirable, before settling on a definite test for use in the laboratory, to make a comparison between results obtained with a number of the tests in general use and those obtained by a test the conditions of which approximated as nearly as possible to actual working conditions. The cells subjected to the various tests were selected not in order to ascertain which type of cell is the best when taken into practical use, but with a view to determining the most suitable method of testing dry cells. The four types chosen for the purpose of the investigation were therefore those which previous tests had indicated as possessing widely different characteristics.

The size of cell employed was that most generally used for telephone work in this country, the dimensions over all being 7 in. × 2½ in. × 2½ in. Sixty cells of the requisite size of each of the four types were kindly made and supplied by the manufacturers.

In order to ensure that all the observations could be commenced at the same time and that the cells should be subjected to exactly similar treatment as regards variations of temperature and time of storing, the makers were asked to deliver the cells on a given day. Further, they were asked to make

them up so that the cells of each make should be as nearly as possible alike.

Four cells of each make were selected at random for each of the discharges mentioned. It was evident from the close agreement between the individual cells in each group that this number could be taken as fairly representative of the type. The four makes of cells are designated on the curves and in the tables A, B, C, and D respectively.

The following series of tests were taken as being representative of those in general use. Such tests as "to short-circuit the cell until it bursts" were not used, it being considered that, although these tests may have some value to the people using them, they could not be expected to afford any useful information for the purposes of this investigation.

Test 1, curve Fig. 1, represents as nearly as possible the working conditions of a cell on a telephone circuit. The information on which this test is based was kindly supplied by the National Telephone Company, *i.e.*, two cells work-

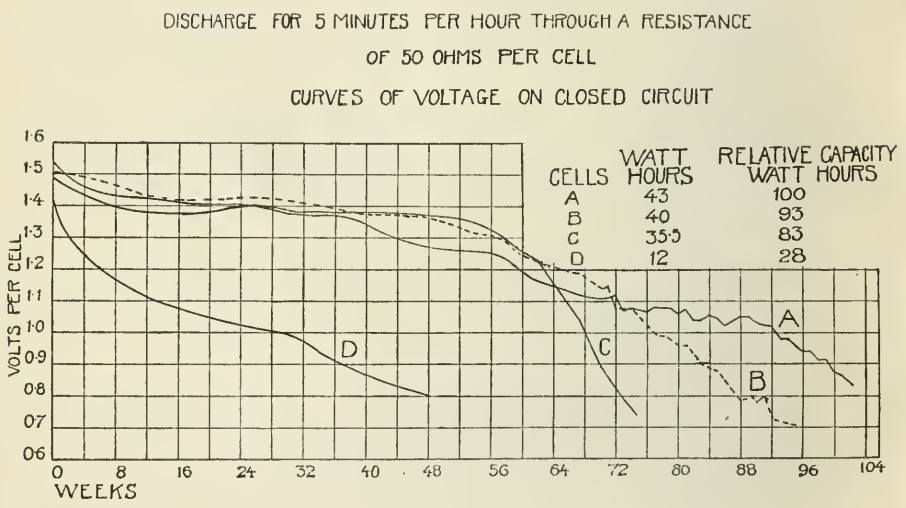


Fig. 1.

ing on a circuit the resistance of which is about 100 ohms and the average discharge five minutes per hour. Measurements were made by the National Telephone Company, and it was found that the minimum current with which a telephone microphone would work satisfactorily was 0·018 ampere, and the discharge of the cells was therefore considered to be completed when the voltage had fallen to 0·9 volt at the end of any period of discharge.

Test 2, curve Fig. 2, discharge for five minutes per hour through a resistance of 1 ohm. This test was introduced in order to see how a discharge, allowing the same periods of work and rest, but at a higher current than the normal, would agree with the results obtained under working conditions.

Test 3, curve Figs. 3A, 3B, 3C, 3D show the results of the test which was specified by the National Telephone Company, the cells in this case being discharged continuously for six hours per day through a resistance of 5 ohms, resting the other 18 hours, resting also Saturdays and Sundays. The discharge in this case was considered to be complete when the voltage of each cell, taken after the period of rest, had fallen to 0·9 volt when discharged for two minutes through a resistance of 50 ohms.

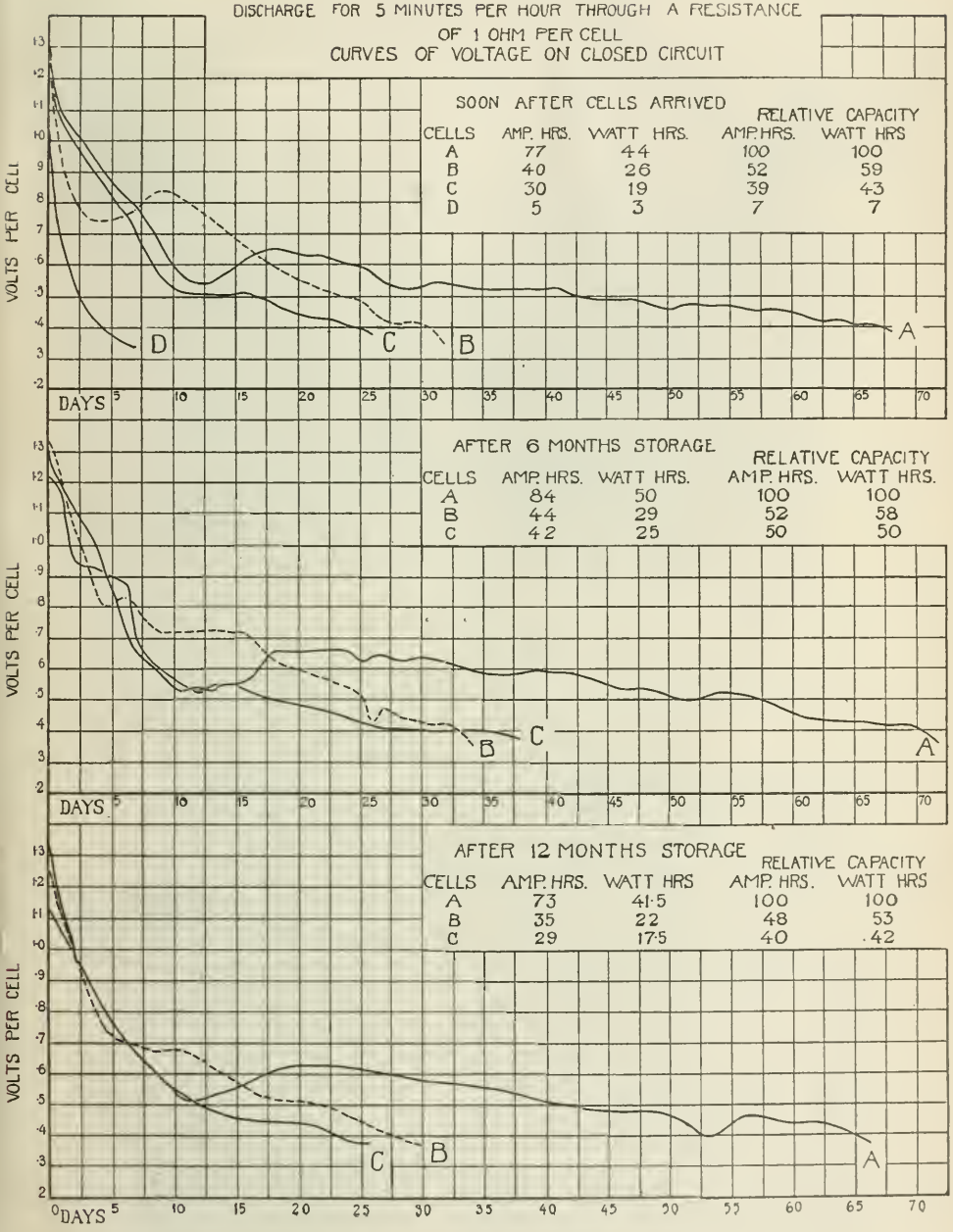

DISCHARGE FOR 5 MINUTES PER HOUR THROUGH A RESISTANCE OF 1 OHM PER CELL
CURVES OF VOLTAGE ON CLOSED CIRCUIT
SOON AFTER CELLS ARRIVED
CELLS AMP. HRS. WATT HRS. RELATIVE CAPACITY AMP. HRS. WATT HRS
A 77 44 100 100
B 40 26 52 59
C 30 19 39 43
D 5 3 7 7
AFTER 6 MONTHS STORAGE
CELLS AMP. HRS. WATT HRS. RELATIVE CAPACITY AMP. HRS. WATT HRS.
A 84 50 100 100
B 44 29 52 58
C 42 25 50 50
AFTER 12 MONTHS STORAGE
CELLS AMP. HRS. WATT HRS RELATIVE CAPACITY AMP. HRS. WATT HRS
A 73 41·5 100 100
B 35 22 48 53
C 29 17·5 40 ·42
VOLTS PER CELL
DAYS
A
B
C
D

FIG. 2.

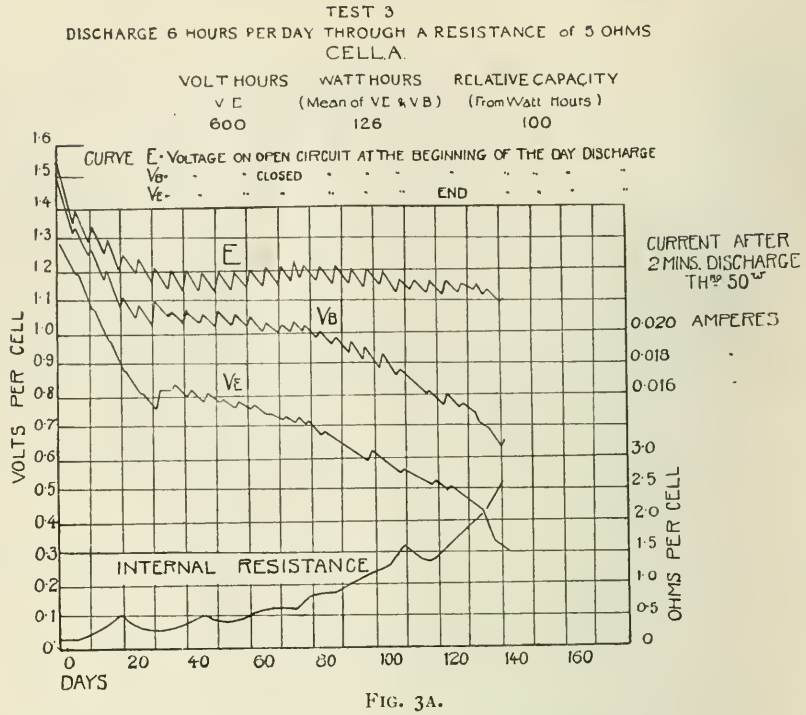

TEST 3
DISCHARGE 6 HOURS PER DAY THROUGH A RESISTANCE of 5 OHMS
CELL A.
VOLT HOURS (V E) 600
WATT HOURS (Mean of VE & VB) 126
RELATIVE CAPACITY (From Watt Hours) 100
CURVE E · VOLTAGE ON OPEN CIRCUIT AT THE BEGINNING OF THE DAY DISCHARGE
VB · · · CLOSED
VE · · · END
E
VB
VE
INTERNAL RESISTANCE
VOLTS PER CELL
OHMS PER CELL
DAYS
CURRENT AFTER 2 MINS. DISCHARGE THRO 50Ω
0·020 AMPERES
0·018
0·016

FIG. 3A.

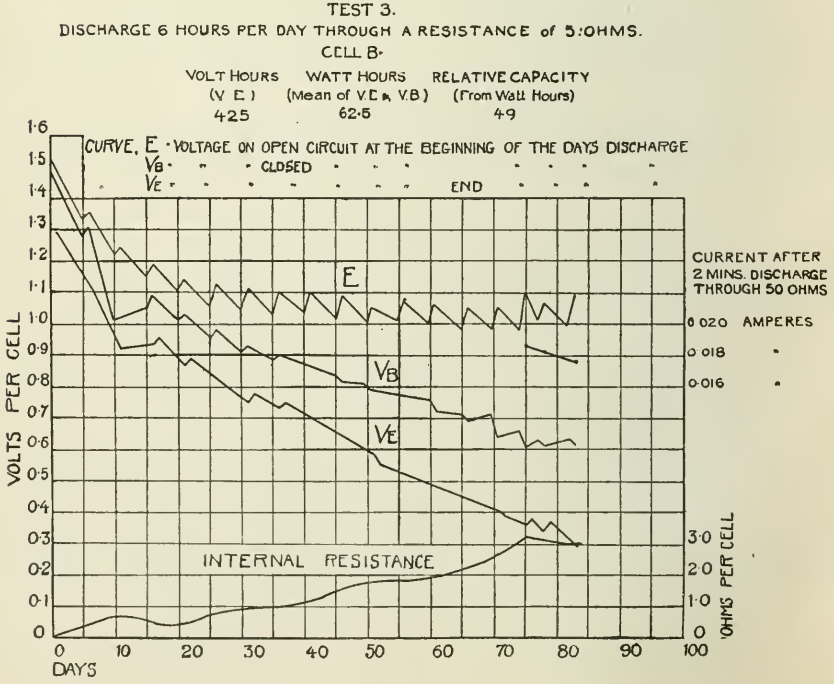

TEST 3.
DISCHARGE 6 HOURS PER DAY THROUGH A RESISTANCE of 5 OHMS.
CELL B.
VOLT HOURS (V E) 425
WATT HOURS (Mean of VE & VB) 62·5
RELATIVE CAPACITY (From Watt Hours) 49
CURVE E · VOLTAGE ON OPEN CIRCUIT AT THE BEGINNING OF THE DAYS DISCHARGE
VB · · CLOSED
VE · · · END
E
VB
VE
INTERNAL RESISTANCE
VOLTS PER CELL
OHMS PER CELL
DAYS
CURRENT AFTER 2 MINS. DISCHARGE THROUGH 50 OHMS
0·020 AMPERES
0·018
0·016

FIG. 3B.

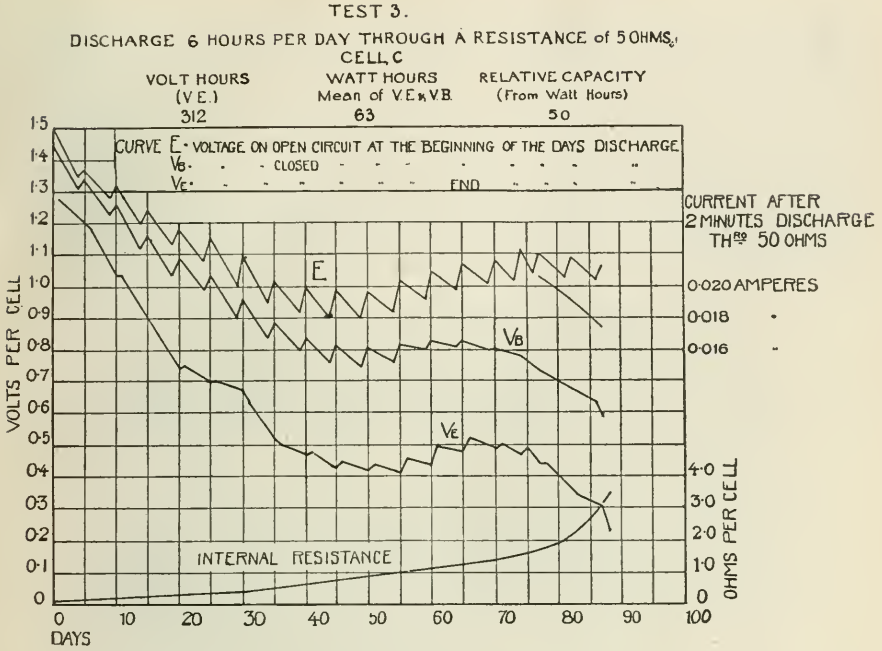

TEST 3.
DISCHARGE 6 HOURS PER DAY THROUGH A RESISTANCE of 5 OHMS.
CELL C
VOLT HOURS (V E.) 312
WATT HOURS Mean of V.E.&V.B. 63
RELATIVE CAPACITY (From Watt Hours) 50
CURVE E - VOLTAGE ON OPEN CIRCUIT AT THE BEGINNING OF THE DAYS DISCHARGE
VB - - CLOSED
VE - - - - - - END
CURRENT AFTER 2 MINUTES DISCHARGE THRO 50 OHMS
0·020 AMPERES
0·018
0·016
VOLTS PER CELL
OHMS PER CELL
INTERNAL RESISTANCE
DAYS

FIG. 3C.

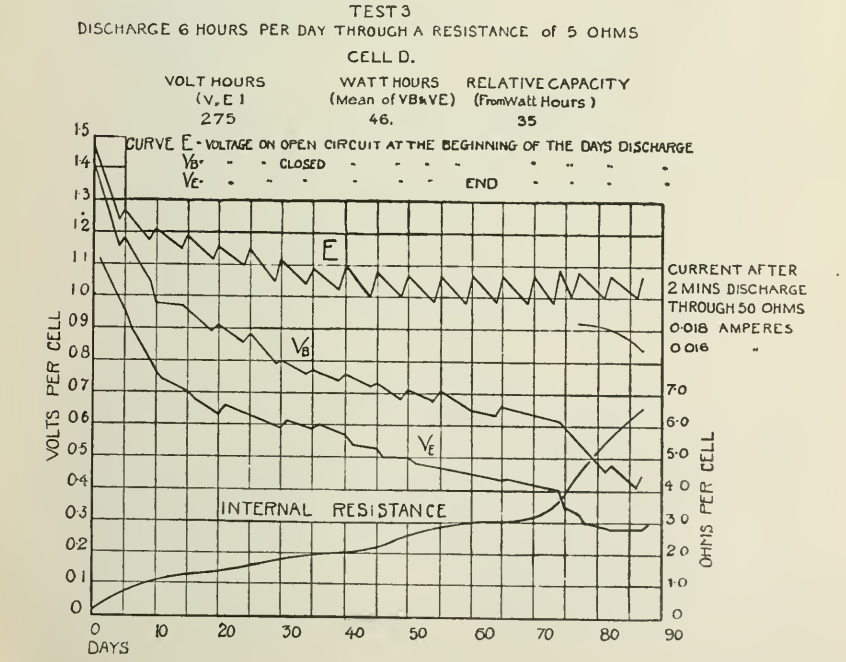

TEST 3
DISCHARGE 6 HOURS PER DAY THROUGH A RESISTANCE of 5 OHMS
CELL D.
VOLT HOURS (V, E.) 275
WATT HOURS (Mean of VB&VE) 46.
RELATIVE CAPACITY (From Watt Hours) 35
CURVE E - VOLTAGE ON OPEN CIRCUIT AT THE BEGINNING OF THE DAYS DISCHARGE
VB - - CLOSED
VE - - - - - - END
CURRENT AFTER 2 MINS DISCHARGE THROUGH 50 OHMS
0·018 AMPERES
0·016
VOLTS PER CELL
OHMS PER CELL
INTERNAL RESISTANCE
DAYS

FIG. 3D.

Test 4, curve Fig. 4, is the test formerly specified by the British Post Office. Each cell was in this case discharged continuously at a constant current (in this case 20 milliampere) until the e.m.f. (voltage on open circuit), observed immediately after the current was switched off, had fallen to one volt.

Test 5, curve Fig. 5, is the test most favoured by manufacturers, each cell being discharged continuously through a resistance of 10 ohms. This test is largely used, but the various users are seldom agreed as to the point at which the discharge should be considered complete. Three complete discharges were made under these conditions; one immediately after the cells were re-

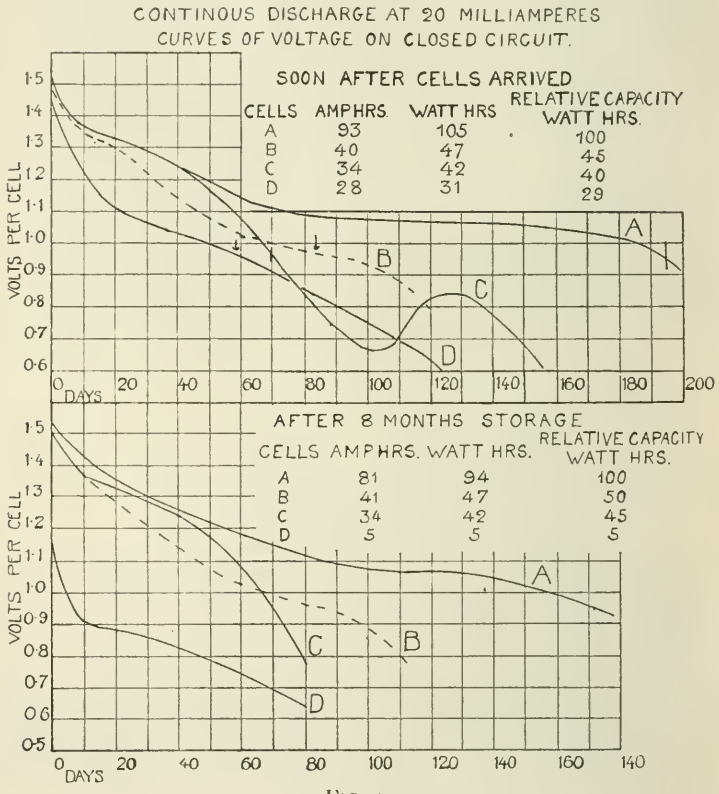

CONTINOUS DISCHARGE AT 20 MILLIAMPERES
CURVES OF VOLTAGE ON CLOSED CIRCUIT.
SOON AFTER CELLS ARRIVED
CELLS AMPHRS. WATT HRS RELATIVE CAPACITY WATT HRS.
A 93 105 100
B 40 47 45
C 34 42 40
D 28 31 29
VOLTS PER CELL
DAYS
AFTER 8 MONTHS STORAGE
CELLS AMPHRS. WATT HRS. RELATIVE CAPACITY WATT HRS.
A 81 94 100
B 41 47 50
C 34 42 45
D 5 5 5
VOLTS PER CELL
DAYS

Fig. 4.

ceived, one after six months' storage, and another after the cells had been stored for twelve months.

Test 6, curve Fig. 6. In this case each cell was discharged through a resistance of 100 ohms, the discharge being considered to be complete when the voltage had fallen to 0·9 volt per cell.

Test 7, curve Fig. 7. This is one of the tests used by the War Office, and consists in observing the voltage of the cell when it is discharged continuously through a resistance of 500 ohms.

Fig. 8. In this case ten cells of each make were stored in a cupboard, observations being taken from time to time of the open-circuit voltage.

Results of the Tests.—The volt-hours, ampere-hours, and watt-hours given

by each cell (the result given being in each case the mean of each group of four cells) and, in addition, the relative value of each set of cells, taking for this purpose the output of cells A as 100, are given on the curves. A summary of the relative values is given in Table I. It will be seen that the order of merit was the same throughout, but the relative capacity varied considerably. The reason for this is apparently due to different methods of manufacture. Cells A gave the greater capacity on all discharges, but whereas B and C were lower only by 7 and 17 per cent. respectively in Test 1, they were more nearly 50 per cent. lower on most of the other tests. In Test 6—discharge through 100 ohms—the results appear to be more nearly normal, while in No. 7, a slower discharge than under normal working condi-

TABLE I.

Relative Capacity of the Cells at Various Rates of Discharge.

(The values are in watt-hours, except where otherwise stated.)

No.		Cells. A.	B.	C.	D.
1	5 mins. an hour on 50 ohms	100	93	83	28
2	5 mins. an hour on 1 ohm initial ...	100	59	43	7
	After 6 months' storage	100	58	50	—
	After 12 months' storage	100	53	42	—
3	6hours per day on 5 ohms—				
	V.E.	100	71	68	47
	Mean of V.B. and V.E. curves ...	100	50	50	35
4	Continuous at 20 milliamperes—				
	Initial ampere-hours	100	43	36	30
	Initial watt-hours	100	45	40	29
	After 8 months' storage, watt-hours ...	100	50	45	5
5	Continuous on 10 ohms—				
	Initial to 0·7 volt	100	75	53	60
	Initial to 0·5 volt	100	76	55	60
	After 6 months' storage—				
	To 0·7 volt	100	59	44	28
	After 12 months' storage	100	67	50	2
6	Continuous on 100 ohms	100	68	51	35
7	Continuous on 500 ohms—				
	To 1·3 volt	100	102	87	10
	To end, *i.e.*, 118 weeks	100	94	—	—

tions, the relative capacity of cell B is nearly equal to that of A. Cell D was consistently much lower than the others with the exception of Test 5, where the relative capacity was about double that which it gave under working conditions. This cell seems best suited by a continuous discharge at a medium rate; with the shorter intermittent discharge No. 2, and the long continuous one No. 7, the capacity was very low, while a comparison of the results shown in Fig. 5, after the cells had been stored for a long period, with those in Fig. 1, seems to show that this particular cell deteriorates more rapidly when idle than when it is discharged intermittently at a slow rate.

Effect of Storage.—The effect of long storage on the capacity of the cells is shown on the curves—Fig. 2 intermittent discharge through 1 ohm, Fig. 4 continuous discharge at a constant current of 20 milliamperes, and Fig. 5 continuous discharge through a resistance of 10 ohms. In the case of cells A a somewhat unexpected result was obtained, the capacity both on Tests 2 and 5

having increased slightly after six months' storage, while after twelve months it was nearly the same as that obtained initially. On the 20 milliampere discharge, however, the capacity after eight months' storage had slightly

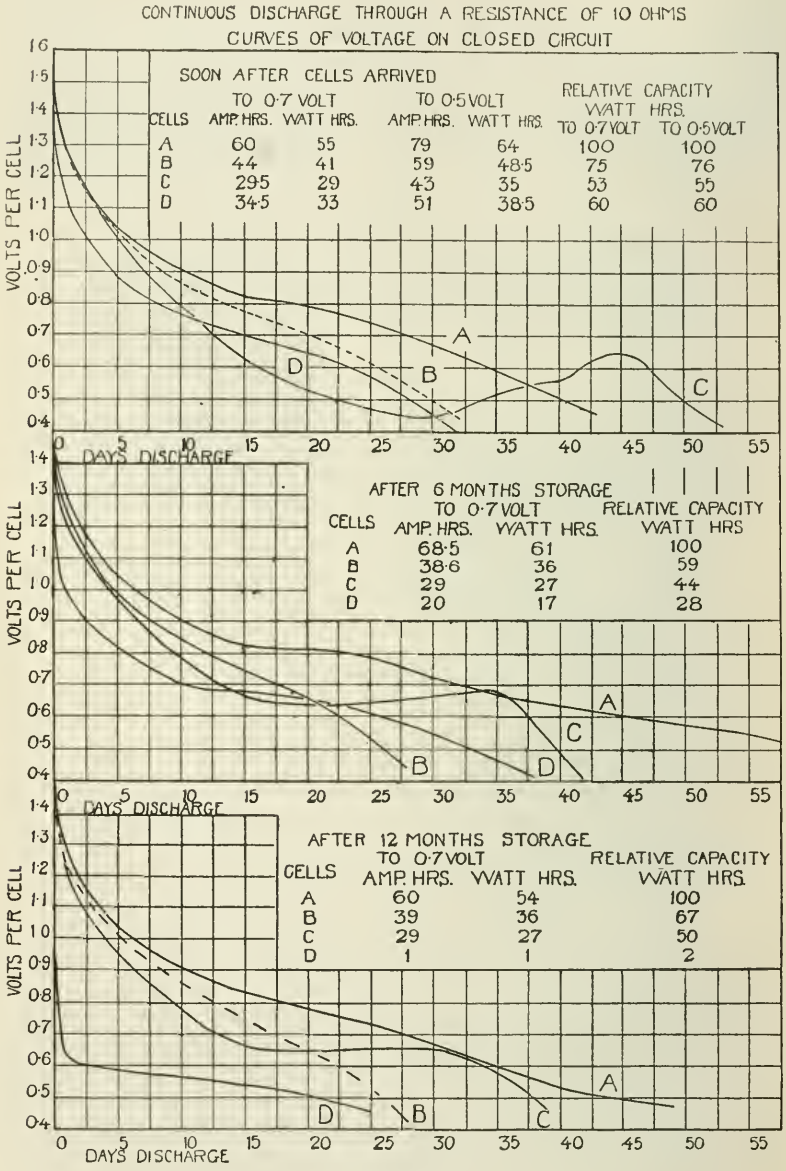

CONTINUOUS DISCHARGE THROUGH A RESISTANCE OF 10 OHMS
CURVES OF VOLTAGE ON CLOSED CIRCUIT
SOON AFTER CELLS ARRIVED
CELLS | TO 0·7 VOLT AMP. HRS. | TO 0·7 VOLT WATT HRS. | TO 0·5 VOLT AMP. HRS. | TO 0·5 VOLT WATT HRS. | RELATIVE CAPACITY WATT HRS. TO 0·7 VOLT | RELATIVE CAPACITY WATT HRS. TO 0·5 VOLT
A 60 55 79 64 100 100
B 44 41 59 48·5 75 76
C 29·5 29 43 35 53 55
D 34·5 33 51 38·5 60 60
AFTER 6 MONTHS STORAGE
CELLS | TO 0·7 VOLT AMP. HRS. | TO 0·7 VOLT WATT HRS. | RELATIVE CAPACITY WATT HRS.
A 68·5 61 100
B 38·6 36 59
C 29 27 44
D 20 17 28
AFTER 12 MONTHS STORAGE
CELLS | TO 0·7 VOLT AMP. HRS. | TO 0·7 VOLT WATT HRS. | RELATIVE CAPACITY WATT HRS.
A 60 54 100
B 39 36 67
C 29 27 50
D 1 1 2
VOLTS PER CELL
DAYS DISCHARGE

Fig. 5.

decreased. The capacity of cells B and C decreased only slightly as a result of long storage, while with cells D the capacity had fallen off greatly, the cells at the end of twelve months being practically useless.

The tests on open circuit shown in Fig. 8, taken over a period of nearly

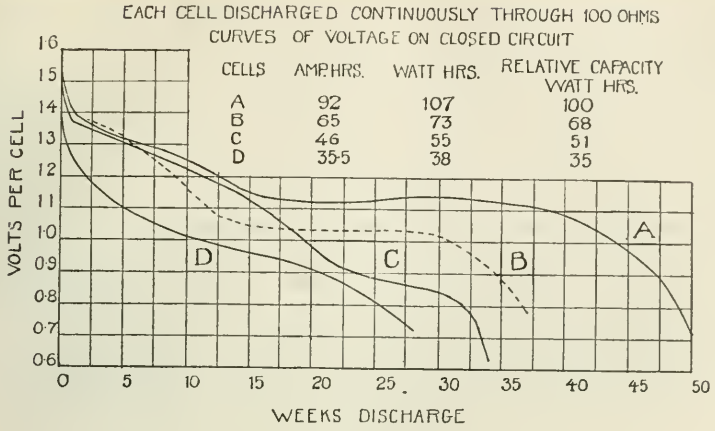


FIG. 6.

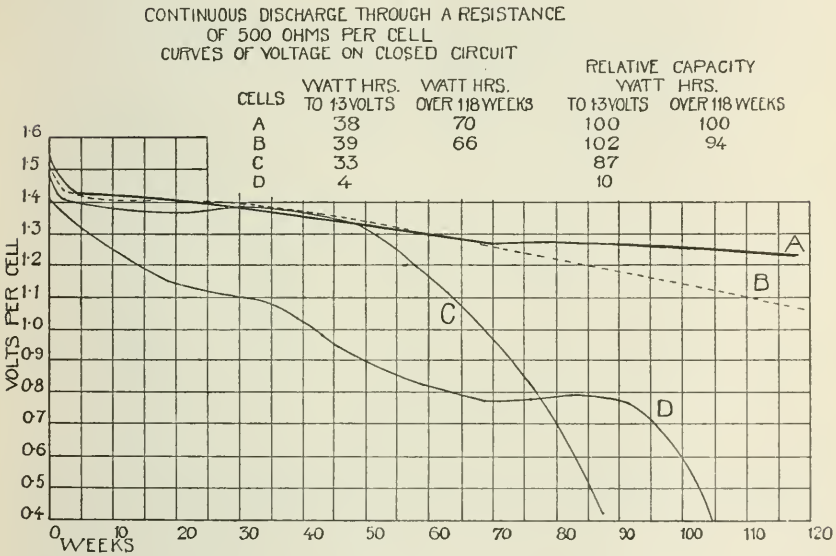

CONTINUOUS DISCHARGE THROUGH A RESISTANCE
OF 500 OHMS PER CELL
CURVES OF VOLTAGE ON CLOSED CIRCUIT
CELLS WATT HRS. TO 1·3 VOLTS WATT HRS. OVER 118 WEEKS RELATIVE CAPACITY WATT HRS. TO 1·3 VOLTS RELATIVE CAPACITY WATT HRS. OVER 118 WEEKS
A 38 70 100 100
B 39 66 102 94
C 33 87
D 4 10
VOLTS PER CELL
WEEKS
A
B
C
D

FIG. 7.

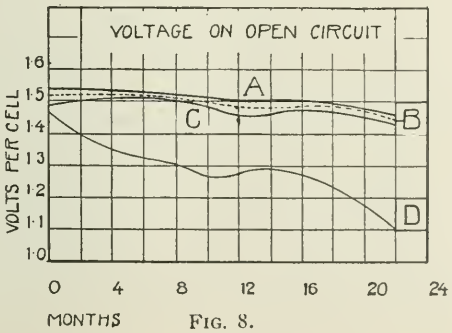


FIG. 8.

two years, show somewhat the same order of change in the cells as in the previous tests, the voltage of A, B, and C having fallen by about 5 per cent. during this period, while that of cells D had fallen by about 25 per cent.

The curious rise in voltage in cells C (Fig. 4) when the cells were approaching the end of their discharge was found to occur with this make of cell in all the tests made at a fair rate of discharge; it occurred, however, in most cases after the voltage had fallen below that at which the discharge was considered complete, and is consequently not shown in all the curves. The rise was found to coincide with the bursting of the zinc box; and while the increase of capacity may seem to commend itself, it should be pointed out that, when the zinc box burst the electrolyte saturated the paper and cardboard cover of the cells, and that the resultant low insulation resistance rendered them useless under working conditions.

Capacity at various Rates of Discharge.—In order to determine accurately the capacity of dry cells at various rates of discharge, it would be necessary

TABLE II.

Relation between Incidence of Discharge and Capacity.

(The capacity in each case is given in watt-hours.)

Test No.	Cells.			
	A	B	C	D
1	43	40	36	12
2	44	26	19	3
3	126	63	63	46
4	105	47	42	31
5	64	49	35	38
6	107	73	55	38
7	70	66	—	—

to fix upon a point at which the discharge should be considered to be complete, at each of the various rates. This point should, of course, be based upon the relation of the fall in voltage to the current which is drawn from the cells. In the present work, which was undertaken more as an investigation of the various tests in everyday use, the limit was in most cases that specified by the various users of cells. Therefore, the summary of the results, given in Table II., must be taken only as an approximation. The differences are, however, in some cases so large that the effect of stopping the discharge at a slightly higher or lower point on the curve would not seriously affect them. For the purpose of this comparison we might dismiss cells D, that type being so different from the others, especially in its keeping properties. It will be seen that cell A gives its greatest watt-hour capacity on Test 3—the intermittent discharge of six hours per day allowing eighteen hours' rest in between each period of discharge; cell C likewise gives its greatest capacity at this discharge, while cell B is better at the slower continuous discharges. Taking the discharges Nos. 4, 5, and 6—all continuous at approximately 0·2, 0·1, and 0·01, amperes respectively—all the cells, as might have been expected, give their greatest capacity at the lower rate of discharge, decreasing in somewhat different degree as the

discharge rate increased. On the intermittent discharge No. 1, however, all the cells gave a lower capacity than when discharged continuously at about the same current. This result is remarkable inasmuch as the cells, A, B and C, tested by the continuous discharges, showed little or no deterioration after twelve months' storage.

Conclusions.

In view of the great difference between the relative results of different makes of cells under the various conditions of discharge, and also as to the relation between the incidence of the discharge and the capacity, it seems obvious that with the exception of No. 1 none of the methods of test investigated can be relied on to give even an approximation of the relative capacity of dry cells or of the output which may be obtained under working conditions. What may be called a "rough idea" of the relative value might perhaps be obtained for telephonic purposes from the results of a continuous discharge through a resistance of 100 ohms, but for a really correct comparison the test should approximate as nearly as possible to working conditions. The author has not made a large number of tests on the larger types of dry cell such as are used for ignition purposes, but from the results obtained with those that have been tested there seems every reason to believe that the conclusions arrived at as a result of this investigation would apply also to them; the rate of discharge being, of course, in proportion to the size of the cell.

A standard test of this sort, although it would of necessity take a considerable time and might at first sight be considered laborious, would eventually show distinctly which brand of cell is the best suited to the requirements and would give a very fair approximation of the cost of the energy used. Moreover, satisfactory mechanical arrangements can readily be made for switching the cells off and on, and it is only necessary then to take readings of the voltage about once a week, at, or near, the end of a discharge period. The observations of voltage on open circuit and of internal resistance—at best somewhat indefinite, and always difficult to interpret—would not be required; the process of recording observations would be therefore much simplified.

Apparatus used for the Tests.—The discharges of the cells for Tests 1 and 2 were made by means of a weight-driven clock, on the minute hand of which was soldered a ∩-shaped piece of copper wire. This wire passed through and made contact between two mercury troughs which were fixed just beneath the dial, and which operated a solenoid relay. This, in turn, operated a number of mercury switches, which completed the circuit of the cells through their respective resistances. The height of the mercury trough was adjustable and was set to give exactly a period of five minutes between the entering and the leaving of the contacts.

For the other tests the apparatus which was described in the Laboratory Report for 1907 was used. It consists of a stand on which are a number of circuits for the cells under test. Each circuit is composed of a switch, slotted contacts for the voltmeter points, and the resistance through which the cell has to be discharged. Where cells are required to be discharged at a constant current a shunt is inserted in the circuit. Across this shunt the voltmeter is connected by means of travelling contact-pieces. The reading on the scale is given direct in milliamperes, and terminals are also provided for the insertion of a regulating resistance.

A Campbell bifilar galvanometer made by Mr. R. W. Paul was used for the voltage measurement; this instrument, owing to its absence of zero creep and to its promptness, is particularly well adapted for the work. The

galvanometer scale was calibrated so that a reading of 100 divisions, *i.e.*, a movement of 20 cm. on the scale, was equivalent to 1 volt. The resistance of the instrument when used as a voltmeter was about 3,000 ohms.

The thanks of the author are due to Dr. Glazebrook for his kind advice and interest in the work, to the National Telephone Company, particularly to Mr. J. Poole, for a great deal of advice and information, to the Post Office for information regarding their methods of test, to the various manufacturers who supplied the cells required for the tests; to Mr. H. C. Booth for assistance in collating the results, and to Mr. F. C. Rogers for his painstaking work in connection with taking and recording the very large number of observations involved.

DISCUSSION.

Mr. W. R. Cooper expressed his interest in the Paper and thought it was very satisfactory that so many different methods should give the same order of merit for the cells. It was difficult to know when a test should be considered at an end. In his own work he had always used the simple test of placing cells on a 10-ohm circuit, and he regarded the tests as finished when the p.d. fell to about half the initial e.m.f.; since the e.m.f. varied somewhat from cell to cell, he took 1·5 volts as an arbitrary value for the initial e.m.f. and cut off at half this value. He would like to ask how the internal resistance was measured; whether cells C, which showed a rise in voltage on bursting, were provided with vent tubes; and whether the author could suggest any explanation of the fact that the capacity was lower on an intermittent than on a continuous discharge. In the United States a short-circuit test was often used, but so far as he knew the nature of the short circuit was never specified. Had the author any experience of this method? He (Mr. Cooper) was glad that the Paper had been read before the Faraday Society, and he regarded it as a valuable contribution to the literature of the subject.

Mr. J. Poole congratulated the author on his work, the results of which would be of great use to users of cells. It was very desirable to have a short accurate test to enable new types of cells to be tested and if merits found put into use as early as possible. As it was at present with the usual test, a contract for the delivery of cells might easily run out before the completion of the test.

He believed it was not usually realised to how great an extent dry cells were in use, and it might be of interest to mention that according to Professor Burgess not less than 40,000,000 dry cells were manufactured in America in 1911. It was possible that the number in this country did not approach this, but he could state that the National Telephone Company used over 300,000 cells last year and larger numbers in previous years.

The tests made by the author were carried out at the instance of the National Telephone Company, who wanted to obtain, if possible, a short time test, which would be authoritative and independent, to indicate the efficiency of various types of cells. It was unfortunate that the results obtained were not altogether satisfactory, but this perhaps was inevitable on account of the inherent difficulties of the case.

There were a few remarks on points of detail which he would like to make. The first paragraph of the Paper referred, he thought, originally to telephone work only.

He should like to ask at what temperature the cells were stored. When cells were working ammonia gas was generated, which carried away moisture and tended to dry the cells and increase the resistance.

The cells under test in the National Telephone Company's test were kept working for six hours a day for five days a week, resting on the other two days.

In his opinion the continuous test was not a suitable one for cells of the Leclanché type, as it gave no chance for recuperation, which is one of the chief merits of any Leclanché cell. The apparently lower results of the intermittent test in some cases as compared with the continuous tests might be explained by the fact that the discharge was over a much longer period and there was therefore much more chance for the drying up effect and for local action.

Although it was not possible to publish the names of the cells, it could be stated that cell D might be taken as the type of cells in use some six years ago, whereas A and B represented types of the best of the most recent cells on the market, a marked improvement due entirely to competition and comparative tests.

In justice to British manufacturers it should be noted that although such a great number of American cells were manufactured the best of them were inferior to the best British cells, according to his experience. It was interesting to note also that in America wet cells had been entirely discarded for telephone work, dry cells being used exclusively.

It was a pity that wet Leclanché cells of different types were not also included in the investigation, and although not strictly bearing on the subject of the Paper, it might be mentioned that one curious and important fact had resulted from the tests made by the National Physical Laboratory, which was, that the efficiency of the agglomerate block type of cell was found to be very low indeed as compared with other types of Leclanché cells, although for a long time it had been generally considered as the most efficient type of such cells. In some cases the comparative figures for watt-hours were of the order of 1 to 7 and for ampere-hours of 1 to 10.

Mr. W. R. Rawlings congratulated Mr. Melsom upon his valuable Paper, which, like all Mr. Melsom's work, would, he was sure, become a text-book on the subject. To him, as a user of dry cells, the Paper contained information of great value, as that furnished by manufacturers did not as a rule include the various conditions of discharge.

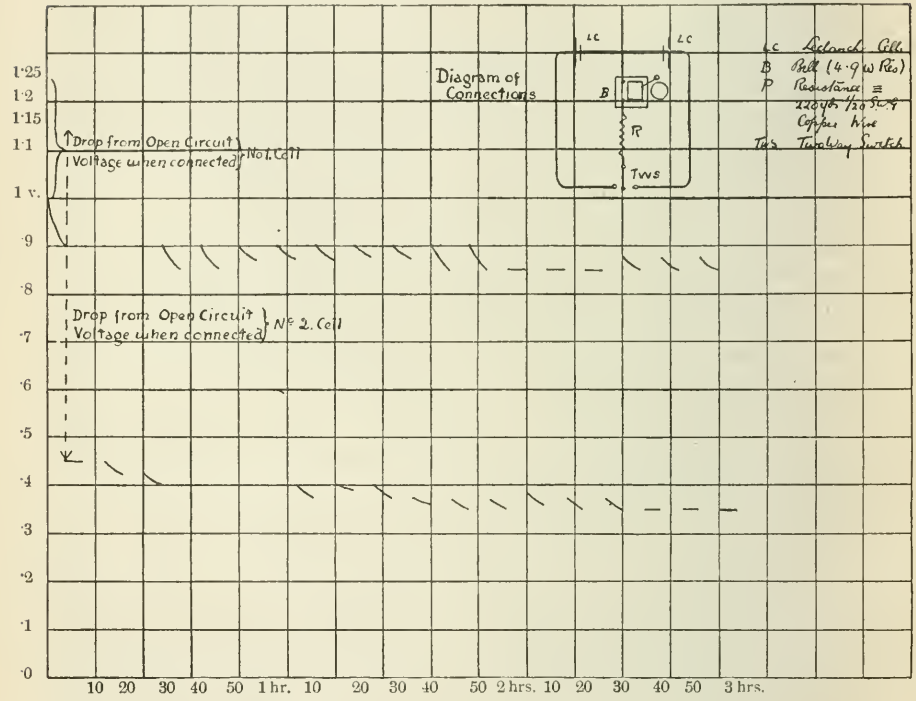
Some time ago he supplied a small lighting installation for a yacht going far North, and as a source of supply he put down half a ton of dry cells. The audience would be interested to hear that the battery supplied fifteen 10 c.p. lamps most efficiently. The unused cells, which were returned after ten months, arrived in good condition. It was true the price worked out at 25s. per unit, but under the circumstances this was cheap, and he recommended the plan to others who might have special small lighting plants to install.

The rise in voltage in dry cells after six months was interesting. A batch of cells which had been accidentally left in the stores three years behaved quite well after that time. It would be interesting to know how long cells actually would be kept. Mr. Melsom had proved that after twelve months the cells had not depreciated.

The facts recorded by the author suggested a use for dry cells which had been overlooked, for example, motor-cars using accumulators for ignition might advantageously carry a dry battery as a stand-by even if it were not used for a year or two.

Finally, he would like to ask Mr. Melsom a question which he was afraid he would not answer, namely, what were the names of the makers of cells referred to in the Paper.

Mr. John D. Mackenzie: A number of years ago I fitted up a rough workshop testing arrangement for testing ordinary Leclanché cells. The annexed diagram shows this arrangement. Two cells taken at random from a batch were connected up as shown through an ordinary electric bell and 220 yards of bell wire, giving a total resistance in circuit of a little over 10 ohms. Each cell was discharged for 5 minutes and resting for 5 minutes. Voltage readings were taken on open circuit, then (*a*) immediately when put into circuit with the bell and (*b*) after discharging for 4 minutes. A few hours per day for two or three days gave a very good idea of the capacity of such cells for regular work. I find that the only figures now in my possession, taken with this arrangement, relate to a method used for regenerating *spent* porous pots.



Two spent porous pots out of the same battery were used, one treated (No. 1) and the other untreated (No. 2). A normal solution of electrolyte was made up and divided equally between the two cells. A series of discharges were taken to find the capacity for work of each cell. The curves annexed show a 3 hours' discharge taken near the completion of test. The open-circuit voltages given were those immediately before putting on load during the particular test. The form of the curves is typical of what I was usually able to obtain from tests taken in this manner, and I never found any reason to doubt that such a test gave a very fair indication of the quality of the cells.

Mr. E. P. Hollis said that Mr. Melsom's Paper was a very welcome addition to the literature on the subject of dry batteries, of which it had been his experience there was a great paucity. Perhaps that must be attributed

to the fact that dry battery making was not one of our great British industries. Some two years ago the American Electrochemical Society had before them two papers on this very subject. In these papers the authors commented on the state of chaos existing in the testing of dry cells. To bring this chaos to order the Society appointed a committee to report on the question and to attempt to formulate some standard tests. He was afraid that the committee had not been able to complete their labours with the consummate ease which they anticipated when they so lightly undertook them. He had scanned the American electrochemical press ever since to find this final report, but he did not think that it had yet been issued. Some time ago there appeared what might be called an interim report, which amounted to nothing more than a confession of failure. The most important result of Mr. Melsom's tests was that he had been able to establish an undoubted superiority of one battery over others in all tests. He had always had an idea that each battery might have a peculiar task at which it was more efficient than other batteries. If the consistency of Mr. Melsom's tests was to be accepted as a criterion of the results likely to be obtained on other tests, this was not so. Apparently, if we found that cell A did better than B on one test, then A would be found to be superior to B on all other tests. Of course, some cells performed better on one test than on another. But when a cell had a superiority over another, that superiority was an all-round one. These tests showed then that it was possible to say with definiteness that one cell was better than another. We could not say that one cell was a given percentage better than another for all purposes. But could we pick up a cell and say, speaking from a knowledge of a test just made upon an identical cell : "This will give me so many coulombs on a certain test ?" He did not think so. The results plotted in each curve were only the averages of a number of tests, and it would be of interest to know what was the range of variations from the average of the individual cells. That was a most important point, for he thought that if he were buying batteries he would be satisfied with a little lower average result if the individual results were less erratic. He had wondered whether a manufacturer would supply a large quantity of cells complying with a specification and be content to submit to a penalty or a bonus whether or not the average discharge or life of a few selected cells fell above or below a specified amount. As to the shelf tests, leaving out cell D he thought that they were very creditable. A drop of less than one-tenth volt in two years was not greatly to be complained at. Still cell D should be a warning to us to be careful of what we were buying. He agreed that a cell should be tested on the work to which it was to be put, and he drew Mr. Melsom's attention to a deserving case for investigation, the cells for use in electric clocks. In the particular clock he had at home a small current is taken every few seconds for a very brief period. He had always been of opinion, probably an offshoot of his experience as an engineer with standing and running machinery, that a little work did a dry cell more good than harm, and the makers of his clock told him that the cells they used were better at this work than standing idle. That might be an exaggeration. At any rate, the first movement of work was not by any means so destructive as the later ones.

Mr. M. Solomon (*communicated*) : I think Mr. Melson is to be congratulated and deserves all our thanks for the very painstaking and laborious experiments which he has carried out. I can only regret, in which regret I think I shall be joined by other manufacturers, that the research has not led to a more satisfactory conclusion. The subject of a standard method of testing dry cells, and indeed all forms of primary cell, is one needing earnest

consideration, because it is beyond question that it is in a state of hopeless confusion at the present time. Every buyer of these commodities who buys in large enough quantities, or considers himself of sufficient official importance to do so, issues a specification of his own, the guiding principle of which appears to be that the essential point is to make it different from everybody else's. In the case of the simpler forms of primary battery many of the large buyers, such as the Government departments and railway companies, think it desirable to specify not results to be obtained but methods of manufacture and nature of materials used. Many of these specifications inflict hardship on certain manufacturers, because they are obviously drawn up on the basis of goods supplied by one or other particular manufacturer. In most cases it is safe to say that it is possible for the manufacturer, whilst rigidly adhering to the specification, to produce an absolutely worthless battery. This is because the users naturally do not really possess the manufacturer's knowledge and cannot include in their specification matters which are really of the first importance but which are not superficially apparent. This in my opinion entirely rules out this method of specifying, and buyers should specify the results to be obtained, leaving the method of manufacture entirely to the manufacturer. This makes it desirable that a standard and simple method of test should be developed. Instead of this, as I have said, each buyer has his own theories which he embodies in his specification. To give only one or two examples, one Colonial Government specifies a test in which the cells are discharged through a resistance of 5·1 ohms, which I can only imagine to be due to the department in question possessing a quantity of inaccurate 5-ohm resistances. Another Colonial Government requires guarantees as to the behaviour of the cells under certain elaborate conditions of test during a period of two years if held in stock in any part of their dominion, a guarantee which of course could not be given by any really conscientious manufacturer.

It is high time that all these diverse specifications were done away with, and a standard method of testing, such as Mr. Melsom has endeavoured to arrive at, should be adopted. The first and most important condition of such a test is, to my mind, that it should be of reasonable duration. Mr. Melsom arrives at the conclusion that the only satisfactory method of test which he has tried is method No. 1, which requires in the case of the A cells all but two years to carry out a test. This I consider fundamentally ridiculous. People do not ask for quotations two years ahead of the time that they want to buy. Imagine what would happen if this were the specified test. The only reasonable way to apply it would be to obtain delivery of, say, 5,000 cells from the manufacturer, place a percentage of them on test, and hold the remainder in stock for two years until the test was completed, when you would be able to tell the manufacturer whether you accepted delivery or not. Business on such lines is, of course, absurd.

It seems to me, therefore, that this test and all similar tests are ruled absolutely out of court for adoption as standard methods. The only test in Mr. Melsom's series which is reasonable from this point of view is test No. 5, where the cells are discharged through a 10-ohm resistance, and where results of practical value are obtained in about twenty to thirty days. It is unfortunate that this test does not give results strictly comparative with those of test No. 1; but the order of merit of different makes of cells is not far different, so that it would seem that this test, perhaps slightly modified, could be adopted in practice. It is obvious, of course, that the cells of make D, as shown by the curves in Fig. 8, are faulty in the respect that they do not keep well in stock, and for this reason show up as faulty on all the tests of long duration.

It is therefore of importance to supplement test No. 5 by another test which will show the keeping powers of the different makes of cells, and by a combination of this test with test No. 5 it would be possible in a few weeks to arrive at definite conclusions as regards different makes of dry cells. I do not think it should be difficult to devise such a supplementary test, which would hasten the effects which occur whilst the cell is being held in stock. If Mr. Melsom would endeavour to find a satisfactory test for this purpose I believe that there would be now no difficulty in devising a satisfactory standard specification for dry cells.

The Chairman, in asking the meeting to accord a very hearty vote of thanks to the author, regretted with him that the best test took so long to carry out. It was no doubt a fact that the only reliable test was to put cells in use under practical conditions, but Mr. Melsom had shown that qualitative short tests could be made if care was taken in the manufacture to ensure uniformity in any particular type of cell. Under the circumstances the only course available was to make a working test of sample cells and to rely on the manufacturers conforming strictly to the method of manufacture used in making up that sample.

Mr. S. W. Melsom (*reply communicated July 2, 1912*)—In reply to Mr. Cooper, the internal resistance of the cells was measured by observing the open circuit voltage E and closed circuit voltage V, and applying the formula $\frac{E-V}{C}$. This method, owing to the fact that the internal resistance of a cell varies largely with the current drawn from it, gives only comparative results.

The cells C were provided with the ordinary vent tubes.

I am very glad that Mr. Cooper remarked on the "short-circuit test." This is a test which originated, and is, I understand, being largely used in America. Testing authorities there, however, deprecate its use except as giving an indication of the condition of a particular cell at any time. I have had occasion to make tests of this sort, and have always used a dead-beat ammeter having a resistance of 0·01 ohm.

Mr. Poole's figures as to the number of dry cells used are most interesting. In answer to his question, the temperature at which the cells were stored was about 65° F.

In reply to Mr. Rawlings, I regret that I am unable to give any information as to the names of the makers of the cells.

Mr. Hollis will no doubt have seen by this time the report of the American Committee to which he refers. From knowledge gained during these and other tests I think one can say fairly definitely that if a given make of cell has been tested, other cells of the same make would give very nearly the same results. In the case of the large number of tests made at various times to the National Telephone Company's specification, it has been found that two tests on a given type of cell made with an interval of two years between them gave results agreeing to within 10 per cent. The results plotted are, as Mr. Hollis points out, in each case the average of a number, *i.e.*, four cells. The differences between the four cells were very small, in the main not greater than 0·04 volt. It should be pointed out, however, that the makers of the cells were especially asked to make them as nearly as possible alike.

I share Mr. Solomon's regret that it has been impossible to recommend a satisfactory short test, and I agree that the number of specifications of test at present issued by various authorities may inflict hardship on conscientious manufacturers.

I do not think that it is suggested anywhere in the paper that the test under working conditions—which in this case, owing to the high quality of cells A, B, and C, took nearly two years to carry out—should be used to check the capacity of batches of cells as delivered. In this connection it should be pointed out that the length of the test depends on the normal working conditions, and the time required for testing, say, an ignition cell would be very much shorter. Further, I should deprecate short check tests for this purpose as being likely to lead to cells being manufactured to pass the tests satisfactorily without due regard to their capacity under working conditions.

Mr. Solomon considers that test No. 5—a continuous discharge through a resistance of 10 ohms—would give satisfactory comparative results in a few weeks. An analysis of the tests made under these conditions, taking the discharge to 0·7 volt, gives the following results :—

Cells.	Capacity—Watt-hours.		Total.	Relative Capacity.	Relative Capacity, Test 1.
	Initial.	After 6 Months' Storage.			
A	55	61	116	100	100
B	41	36	77	66	93
C	29	27	56	48	83
D	33	17	50	43	28

It is true that the order of merit for the cells is the same as under working conditions, but a comparison of the relative capacities given on the 10-ohm test with those on test 1, *i.e.*, working conditions, shows that cells D give very much better results than under working conditions, while cells B and C are very much worse. The differences amount to as much as 30 per cent., and this when the test is made to cover a period of seven months. I am of opinion that this degree of accuracy is not sufficient for large users of cells, and I very much doubt whether it would be good enough for manufacturers, particularly if cells such as B and C were rejected by a user on the ground that they did not give sufficient output under his conditions of test. Taking into consideration the large difference in the capacity of the cells under the various methods of test, it was not possible, in my opinion, to arrive at any other conclusion than that the only really satisfactory test is one that approximates to working conditions. There is no doubt, of course, that such a test as a continuous discharge through 10 ohms will afford a certain amount of information, though it must not be relied upon as giving more than an indication of the comparative values of cells. Mr. Solomon considers that such a conclusion is ridiculous, but while on this subject his opinion must necessarily carry a great deal of weight, it would have been better if he had given some figures from the many hundreds of tests which he must have made to justify his statement that a 10-ohm test similar to my No. 5 will give satisfactory comparative results in a few weeks. In this connection it is interesting to see that the Committee of the American Electrochemical Society, in their report presented to a meeting in Boston on April 18–20 of this year, arrive at practically the same conclusions as I have. In view of Mr. Solomon's criticisms, I may perhaps be allowed to quote from this report and the investigations on which it is based.

"*Service Test recommended for Cells for Telephone Service.*—Discharge three cells connected in series through 20 ohms resistance for a period of two

minutes each hour during twenty-four hours per day and seven days per week until the closed circuit voltage of the battery at the end of a period of contact falls to 2·8 volts.

"*Miscellaneous Services.*—In addition to the telephone and ignition services, which are by far the most important services in which dry cells are used, there are numerous other services, among which may be mentioned the operation of automobile horns, sewing machine motors, small fans, toys, massage vibrators, cigar-lighters, bells, buzzers, &c. In the aggregate these miscellaneous services consume enormous numbers of cells, but they are so numerous and there are such variable conditions prevailing in each kind of service, that it would be useless to attempt to develop standard tests covering them.

"It is not difficult for any one particularly interested in any special service to arrange a suitable test for himself. Care should be taken to make the conditions of test, viz., number of cells, resistance in circuit, period of drain, &c., approximate those of the service in question."

The report which has been quoted above is based largely on the work of several observers who have at various times contributed papers on the subject, and notably that of D. L. Ordway, whose paper on "The Characteristics of the Modern Dry Cell"* contains the following: "Following the short circuit current test came the continuous resistance test, and it was a long step in advance when it was used. . . . This led to an examination of the conditions obtaining in actual service, and it was soon seen that it was only by devising a test which would as nearly as possible duplicate the conditions under which cells were used that data for their positive value for a given service could be obtained."

It seems likely that the standard test might be shortened somewhat by discharging the cells on a lower resistance, say 20 ohms per cell; the results obtained with test No. 2, however, show that when the resistance is very low the results are valueless.

* *Trans. Amer. Electrochemical Society*, vol. **17**, 1910, p. 358.

CONTRIBUTIONS TO THE KNOWLEDGE OF LIQUID MIXTURES—I.

PROPERTY-COMPOSITION CURVES AND THE MOLECULAR CHANGES WHICH TAKE PLACE ON FORMING BINARY LIQUID MIXTURES.

By ROBERT BECKETT DENISON, M.A., D.Sc., Ph.D.

(*A Paper read before the Faraday Society, Tuesday, March 26, 1912,* Mr. Alexander Siemens, Vice-President, *in the chair.*)

If the numerical value of any physical property of a binary mixture be plotted as ordinate against the fractional composition of the mixture as abscissa, curves are obtained which we will call property-composition curves. In the case of most gases at ordinary temperatures and pressures, the curve is a straight line. We will regard as an ideal binary mixture one which conforms to this simple mixture law. Viewed from a molecular standpoint, an ideal binary mixture is one in which both kinds of molecules are entirely in the same state after mixing as they were before. There is, in fact, no molecular change on mixing.

For liquid binary mixtures the property-composition curves are not generally straight lines. Some few liquid mixtures have been discovered which obey the straight-line law, but they are decidedly the exception rather than the rule. It is of interest to note that the constituents of such liquid mixtures are always chemically similar, and no chemical combination between them would be expected. The usual types of curve for liquid binary mixtures are—

1. Sagged curves.
2. Curves with a maximum or a minimum.

It has been generally assumed that there must be some molecular change on mixing two liquids if such curves are obtained instead of a straight line, but there does not seem to be a consensus of opinion as to which type of curve corresponds to a given molecular change.

As instances of molecular change on mixing, one would expect—

1. Association of one or both components.
2. Dissociation of one or both components.
3. Chemical combination between the components of the mixture.

All three processes have been assumed to take place in different cases to "explain" the divergence from the straight-line law.

Dunstan, in a study of the viscosity of liquid mixtures,* writes in

* *J.C.S. Trans.*, 1904, 821.

reference to mixtures of alcohol and acetone : "Since both these compounds belong to the associated type of substances, a curve such as that given by alcohol-water mixtures, resulting in a well-formed maximum, would be expected." From this statement it appears that the author attributes a maximum in the property-composition curve to a process of molecular association. Other investigators attribute such maxima to chemical combination between the components of the mixture. Dunstan similarly connects the occurrence of a minimum with a process of dissociation.* Quite another standpoint is taken by Holmes,† who attributes volume changes on mixing liquids entirely to purely physical molecular changes. It is thus evident that there is a considerable difference of opinion as to the cause of liquid mixtures not conforming to the straight-line law. There seems to be but little evidence for connecting a given type of property-composition curve with a process of association or dissociation. The same can, however, hardly be said of chemical combination. It has been observed that those liquid mixtures which have a maximum in their property-composition curve are generally formed with evolution of heat and with volume alteration. This in itself was often considered sufficient to indicate the nature of the process taking place ; but when the maximum in the property-composition curve coincides with a simple molecular relationship between the amounts of the two components (as it sometimes does), it seems only natural to deduce the formation of a compound whose formula is given by the position of the maximum.

So often does this method of detecting combination in solution appear in chemical and physical literature, that its somewhat arbitrary nature cannot be too clearly pointed out. If it were always the case that the maximum in the curve corresponded with simple molecular proportions of the constituents, then it must be admitted the claims of the method for determining chemical composition in solution would be too strong to be neglected. This is, however, by no means always the case, and further, the position of the maximum has been found to vary with external conditions, *e.g.*, temperature.

The supporters of the chemical combination theory had to "explain" this variation by another assumption, viz., that the compound dissociates on heating. However likely this may be, the fact remains that up to the present it has been found impossible to demonstrate the presence of either the chemical compound or the process of dissociation. Owing to the number of assumptions involved, most chemists have abandoned this method of arriving at the formula of compounds in solution. Some go further, and are not inclined to believe in the possibility of deducing the formula or even the formation of compounds in solution from a study of the physical properties of liquid mixtures. Washburn, in a recent review,‡ sums up the position as follows :—

"We are therefore forced to conclude, in spite of the extensive literature on this phase of the subject, that methods of studying hydration which depend upon the deviations of any physical property of a solution from the law of mixtures are incapable of yielding any conclusive information regarding the complexity or even the existence of hydrates in aqueous solution."

Although one feels that one must agree with this conclusion upon the evidence as yet brought forward, still, it would seem that there must be some connection between the physical properties of liquid mixtures and the formation of a chemical compound between their components. Almost the

* *J.C.S. Trans.*, 1905, 11. † Ibid., 1906, 89, 1774.

‡ "Hydrates in Solution," *Tech. Quart.*, xxi., 1908.

very first definition learned by a student of chemistry is that the physical and chemical properties of a compound differ from those of a corresponding mixture. It would seem then that it only remains to find out how this difference in property is to be connected with the formula and the amount of the compound produced. Any such connection must, of course, fit in with acknowledged chemical laws, and, if possible, be capable of quantitative numerical treatment.

This is the object of the present paper.

In attempting to connect the form of property-composition curves with definite molecular processes, it would seem advisable in the first place to assume that a given process takes place, and then to deduce the corresponding property-composition curve.

Let us take as our starting-point the assumption that the law of mixtures, *i.e.*, the straight-line relationship, would hold for binary liquid mixtures if there were no molecular change on mixing. If, then, molecular change does take place, be it association, dissociation, or chemical combination, the result is that our mixture consists of at least three molecular species instead of the original two. The deviation from the mixture law is then due to the new kind of molecules present, and it cannot be far from the truth to put the deviation proportional to the number of new molecules formed. We shall see later that it must be so in the case of chemical combination taking place, and for the present then we will assume that in binary mixtures, where a molecular change takes place on mixing, the deviation from the mixture law is proportional to the number of new molecules formed.

Suppose we consider the case of a mixture of water and another liquid whose molecules we will denote by A_2. We will assume that on mixing the two liquids dissociation of A_2 takes place according to the equation—

$$A_2 \rightleftarrows 2\,A.$$

The water takes no part in the reaction, but simply acts as a diluent. The greater the proportion of water present, the greater must be the degree of dissociation, owing to the principle of mass action. Suppose we have a mixture of y mols of the substance A_2 and $(1-y)$ mols H_2O, and let the degree of dissociation of A_2 in the mixture be γ.

We have then in the system—

$$\begin{array}{rl} y\,(1-\gamma) & \text{mols free } A_2 \\ 2\,y\,\gamma & \text{,,} \quad \text{,,} \quad A \\ (1-y) & \text{,,} \quad \text{,,} \quad H_2O \end{array}$$

The total number of mols is now $(1+y\gamma)$.

Putting the active mass of each molecular species equal to its fraction of the total mols present, we have—

$$\frac{y(1-\gamma)}{1+y\gamma} = K\left(\frac{2y\gamma}{1+y\gamma}\right)^2$$

or—

$$(1-\gamma)(1+y\gamma) = 4Ky\gamma^2$$

By putting $y = 0{\cdot}1$, $0{\cdot}2$, &c., successively, and assigning a definite value to K, we can of course calculate the number of mols and the active mass of each molecular species present. For the sake of simplicity I have taken

$K = 1$, and calculated the numbers given in Table I. From these numbers the curves shown in Fig. 1 have been constructed. They show the variation

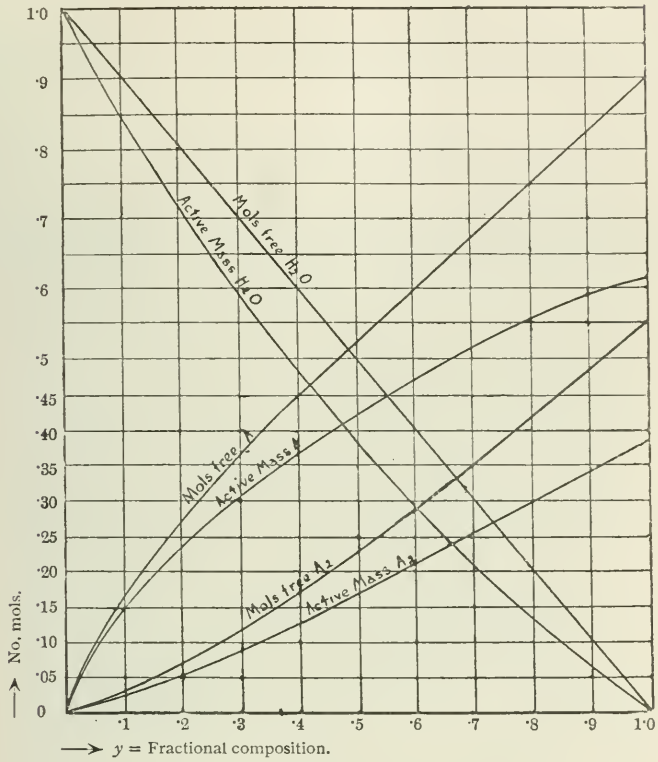


FIG. 1.

in the number of mols and in the active mass of the different substances present as y increases from 0 to 100 per cent. of the mixture.

TABLE I.

y.	γ.	Mols free A_2 $=y(1-\gamma)$.	Mols free A $=2y\gamma$.	Mols free H_2O $(1-y)$.	Total Mols $1+y\gamma$.	Molar Fractions.		
						A_2.	A.	H_2O.
0	1·00	0	0	1·00	1·00	0	·0	1·00
·2	0·677	·065	·271	·80	1·136	·057	·239	·704
·4	·573	·171	·458	·60	1·229	·139	·372	·489
·6	·514	·292	·617	·40	1·309	·223	·471	·306
·8	·476	·419	·762	·20	1·381	·304	·551	·145
1·0	·447	·553	·894	0	1·447	·382	·617	0·00

It is evident from these curves that neither the number of mols of the new kind of molecule nor its active mass reaches a maximum or a minimum value at any composition of the mixture y. Such a maximum or minimum cannot be conceived owing to the continual increase in the degree of

dissociation as the active mass of the water increases. Moreover, the equation $(1-\gamma)(1+y\gamma)-4Ky\gamma^2=0$, on differentiation with respect to y, gives no maximum or minimum value of $(y\gamma)$ for positive fractional values of both y and γ.

Having now obtained the molar fraction of each kind of molecule present in the mixture, we can construct property-composition curves in the following manner.

Assuming the law of mixtures that

$$X_M = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3,$$

where X_M is the value of the (molecular) property for the mixture, X_1, X_2, X_3, are the values of the same for the different molecular species present, and β_1, β_2, β_3, represent the molar fractions, *i.e.*, the active mass of each kind of

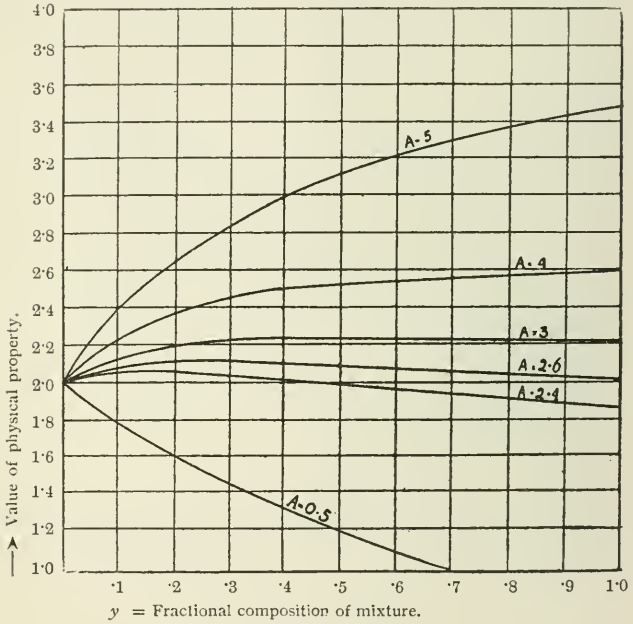


FIG. 2.

molecule, then by assigning arbitrary values to X_1, X_2, and X_3 we obtain values for X_M for the known values of β_1, β_2, and β_3. These values, when plotted against y, give us the required property-composition curve.

The curves in Fig. 2 have been constructed in this way by giving the following values to the constants :—

$$X_{A_2} = 1{\cdot}00,\ X_{H_2O} = 2{\cdot}00,\ X_A = 0{\cdot}5,\ 2{\cdot}4,\ 2{\cdot}6,\ 3{\cdot}0,\ 5{\cdot}0.$$

The curves obtained are mostly of the sagged type, but when X_A has a value very near 2·5, the property-composition curve exhibits a faint maximum.

It would appear, then, that as a general rule a process of dissociation in a binary liquid mixture will give rise to a sagged property-composition curve. Although faint maxima and minima are possible, still a decidedly sharply-formed maximum or minimum seems inconceivable. This is owing to the

fact that the new kind of molecule resulting from the dissociation can never attain a maximum or minimum concentration in the system. The form of the property-composition curve depends not only on the amount of the new molecular species present, but also on the value of the molecular property of the same. Still, it will only be in very peculiar cases where the value of the physical property is such that the resulting property-composition curve exhibits a maximum or minimum.

Let us consider the numbers in Table I. a little further. It will be seen that, provided K remains unchanged when the system contains no water at all, *i.e.*, when $y = 1$, the pure liquid A_2 is itself dissociated. In our case, where $K = 1$, the degree of dissociation when no water or other liquid is present is 44·7 per cent. Thus our so-called pure substance itself consists of two kinds of molecules, and this must be the case to a greater or less degree with all substances which undergo dissociation on mixing with another liquid.

The value of the molecular property of the mixture when $y = 1$, $X_{A_2} = 1$, $X_{H_2O} = 2$, $X_A = 3$, would be 2·233.

If there were no dissociation in the original pure liquid, the value of the property when $y = 1$ would be 1·00. The line joining the points (on the property axes) 2·00 and 1·00 is the straight line which would represent the molecular property for all mixtures of A_2 and H_2O were there no other molecules present.

According to our previous assumption, the number of mols of the product of dissociation (A) should be proportional to the deviation of the actual property-composition curve from the above straight line. The test of this is shown in the following figures. Within experimental error the number of mols of A present can be represented by the deviations from the straight line. For the value of $A = 3$ we have the following figures :—

$y =$	·2	·4	·6	·8	1·0
no. mols A $(2y\gamma) =$	·271	·458	·617	·762	·894
deviation from straight line $(\delta) =$	·382	·633	·848	1·047	1·233
$\frac{2y\gamma}{\delta} =$	·709	·722	·726	·728	·723

Mean $\frac{2y\gamma}{\delta} =$ ·725

Apart from the value when $y = ·2$, the numbers give a more than satisfactory proportionality between number of mols A and the deviation from the straight line (δ).

Granting this proportionality, we can of course calculate the number of mols A in the system from the deviations from the straight line, and thus evaluate the dissociation constant K.

Putting $2y\gamma = x = p\delta$, where—

$2y\gamma =$ No. mols A,

$\delta =$ deviation from the straight line,

$p =$ a constant—

we have, on substituting for γ in the mass action equation—

$$4y - 2x(1 - y) = (4K + 1)x^2.$$

For another value of y, we get

$$4y_1 - 2x_1(1 - y_1) = (4K + 1)x_1^2 ;$$

whence—

$$\frac{4y - 2p\delta\,(1 - y)}{4y_1 - 2p\delta_1\,(1 - y_1)} = \frac{\delta^2}{\delta_1^2}.$$

Everything is known except p. The different values of y and δ give us a number of equations, each two of which gives a value for p. The mean value of p by multiplication with δ gives of course x, the number of mols A formed. In our case we get a mean value of $p = 0{\cdot}72$, whence the following values of K are calculated. The correct value of K of course is unity. These differences from 1·00 are due to approximations in the calculation.

$y =$	·2	·4	·6	·8	1·0	
$\delta =$	·382	·633	·848	1·047	1·233	
$2y\gamma = x =$	·274	·456	·612	·756	·891	
$K = \frac{(1 - \gamma)\,(1 + y\gamma)}{4y\gamma^2} =$	0·96	1·02	1·02	1·01	1·00	Mean 1·00

With regard to the process of association taking place when one liquid is mixed with another, it would seem that there is a theoretical difficulty. Supposing a liquid A on mixing with another undergoes association, forming molecules $(A)_n$, then for every mixture the law of mass action demands—

$$\frac{C_{A\,n}}{(C_A)^n} = K.$$

As the amount of the liquid added to A increases from 0 to 100 per cent. of the mixture, the concentration of A measured by its molar fraction must continue to become less, approaching zero when no A molecules are present. Hence also the concentration of the associated molecules must continually decrease. The result is that no associated molecules can be present in the mixture unless they were originally present in one of the pure components. In short, what takes place is a further dissociation of the already partially associated component. Further association on mixing with another substance (not containing one of the products of the dissociation) is impossible.

Chemical Combination in Solution.—Before we can hope to make any progress in the attempt to connect the process of chemical combination between the components of a binary mixture with the form of the property-composition curve, it is necessary to decide whether any number of such compounds can co-exist in the presence of the pure components, or whether the number is limited. Since the system is supposed to remain homogeneous, the phase rule cannot afford us much help, and we will therefore consider first a corresponding gaseous equilibrium and endeavour to draw some conclusion therefrom.

Let us imagine a mixture of nitrogen and oxygen in true equilibrium at such a temperature that combination between the two elements is possible. Such a condition is, of course, easily attainable, and the equilibrium has been the subject of detailed examination. It is not found to be possible for all the various oxides of nitrogen to co-exist in equilibrium with the two components, nor would any one expect this from *a priori* considerations. We can of course obtain systems consisting of N_2, O_2, and NO, or NO, O_2, NO_2, or NO_2, O_2, N_2O_5, according to the conditions.

The reason why the various oxides cannot exist simultaneously in equilibrium in the presence of the two elementary gases is that the different compounds have widely different energy contents. To put the matter in another way, the dissociation tendencies of the various compounds are so different that they cannot all co-exist in equilibrium in finite amounts. In the presence of free O_2 and free N_2 one compound must largely predominate, but when the active mass of either component becomes very small then another compound is able to exist in finite concentration.

It is probably similar in the case of hydrates in solution, and all compounds formed in binary liquid mixtures. In the case of hydrates, each one must have a dissociation pressure of water vapour which varies with temperature, pressure, and concentration. The aqueous vapour pressure of the hydrate must be in equilibrium with the total aqueous vapour pressure of the system, and if the dissociation pressures of the hydrates differ widely, as one would expect, then their amounts in the system, in the presence of the two components, must also differ widely. That is, in the presence of the two components one compound must largely predominate.

Whether this reasoning be sound or not, the fact remains that if we allow the co-existence of an indefinite number of compounds in the presence of the two components of the mixture, the system becomes incapable of treatment on the lines of mass action. If, however, the number is limited, as pointed out above, then the law of mass action can be applied with some result.

Let us consider one gram of a binary mixture consisting of z grams total A, $1-z$ grams total B, and let there be formed x grams of a compound AB_n, according to the equation

$$A + nB \rightleftarrows AB_n.$$

If the molecular weights of A and B are respectively M_1 and M_2, then

$M_1 + nM_2$ grams of compound contain M_1 grams A

$\therefore$ x „ „ „ $\frac{M_1}{M_1 + nM_2}x$ „ „

Similarly—

x „ „ „ $\frac{nM_2}{M_1 + nM_2}x$ „ B

$\therefore$ 1 gram of the mixture really consists of—

$$\left[z - \frac{M_1}{M_1 + nM_2}x\right] \text{ grams A,}$$

$$\left[1 - z - \frac{nM_2}{M_1 + nM_2}x\right] \text{ grams B and } x \text{ grams } AB_n.$$

If

$$\frac{M_1}{M_1 + nM_2} = a$$

we have—

$$\left.\begin{array}{rl} z - ax & \text{grams A} \\ 1 - z - (1-a)x & \text{„ B} \\ x & \text{„ } AB_n \end{array}\right\} \text{total, 1 gram.}$$

If now S represents any specific physical property of the solution which is applicable to the law of mixtures (*e.g.*, specific volume), and S_1, S_2, S_3

represent the same for A, B, AB_n respectively, we have, according to the law of mixtures—

$$S = (z - ax)\,S_1 + \{1 - z - (1 - a)x\}\,S_2 + xS_3.$$

If now S^1 represents the value of S for the mixture, on the assumption that the simple mixture law held good, *i.e.*, that $x = 0$, then—

$$\begin{aligned} S^1 &= zS_1 + (1 - z)S_2 \\ \therefore S^1 - S &= axS_1 + (1 - a)xS_2 - xS_3. \\ &= x\{aS_1 + (1 - a)S_2 - S_3\} \\ &= x \times \text{a constant for any given mixture.} \end{aligned}$$

Hence the deviation from the simple mixture law is proportional to the amount of compound formed. The actual deviation, *i.e.*, the form of the property-composition curve, depends not only on the amount but also on S_1, S_2, and S_3, the value of the property in question for all three kinds of molecules present. If at any composition of the mixture the deviation from the straight line becomes a maximum, then at this same composition the amount of compound formed must also reach a maximum.

It is important to bear in mind that in this connection the fractional composition of the liquid must be plotted. If one plots as abscissa the number of mols B per 1 mol A in the mixture, then of course the amount of compound formed can only reach a maximum according to the law of mass action when the number of mols of B becomes infinitely great, *i.e.*, when A is completely converted into compound.

It is now necessary to investigate the relation between the composition of the mixture at the point of maximum amount of compound in solution and the formula of the compound.

Let us imagine that we could isolate the compound AB_n free from excess of either A or B. The resulting liquid may be more or less dissociated into A and B, but we will assume there is no excess of either above the amounts demanded by the equation $AB_n \rightleftarrows A + nB$. To this liquid we will now add excess of pure A. In doing so we are performing two operations which affect the equilibrium. Firstly we are adding one of the products of dissociation and so increasing the actual amount of compound formed, and in the second place we are increasing the volume of the system and so decreasing the concentration of the compound. Exactly the same takes place if excess of B be added, and, since the dilution effect is the greater, it would appear probable that the concentration of the compound is a maximum when the whole system has the same percentage composition as the compound itself.

To investigate this further, suppose our mixture consists of y mols total A, and $(1 - y)$ total B, and let there be formed x mols of the compound AB_n. In the equilibrium we have then—

$$\left.\begin{array}{rl} (y - x) & \text{mols free A} \\ 1 - y - nx & \text{,, ,, B} \\ x & \text{,, ,, } AB_n \end{array}\right\} \text{total } (1 - nx) \text{ mols.}$$

If V is the volume of the system, we have by the law of mass action—

$$(y - x)\,(1 - y - nx)^n = KV^n x.$$

The volume unit of concentration is, however, somewhat unsatisfactory for our purpose, since V must be a function of y. This is, of course, necessary owing to the different specific and molecular volumes of A and B. For purposes of differentiation it is not advisable to have more than two variables in the above equation.

By putting the active mass equal to the molar fraction, however, this difficulty is avoided, and we have then—

$$(y - x)(1 - y - nx)^n = Kx(1 - nx)^n.$$

Differentiating with respect to y, we find that x is a maximum when

$$y = \frac{1}{n+1}$$

But $y = \frac{1}{n+1}$ is the fractional molecular composition of the compound AB_n. Hence if chemical combination takes place between the components of a binary mixture, the number of mols of the compound formed must reach a maximum when the mixture as a whole has the same composition

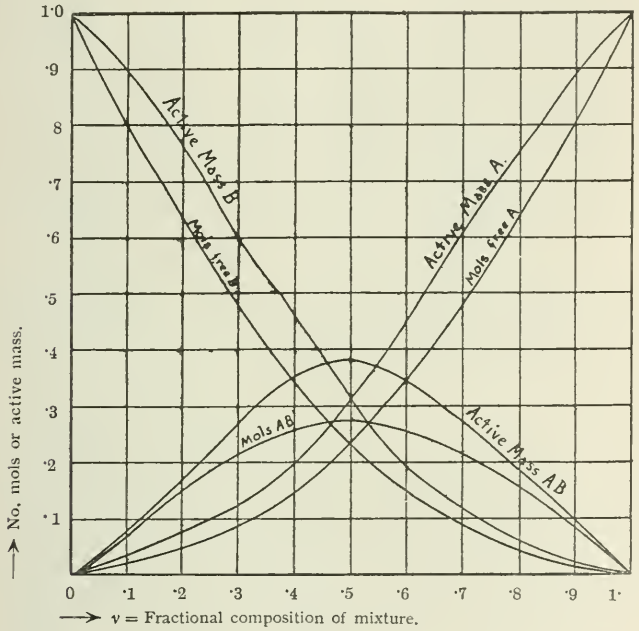


FIG. 3.

as the compound. It has, however, already been shown that the deviation of the property-composition curve from the straight line is also proportional to the amount of compound formed. *Therefore the maximum deviation from the straight line must occur at a composition of the mixture which represents the formula of the compound formed.*

It is interesting to note that the position of this maximum is quite independent of the degree of dissociation of the compound in solution, since the condition for maximum x, $y = \frac{1}{n+1}$, is independent of the equilibrium constant K. We shall see, however, that we can obtain a rough idea of the degree of dissociation, of the compound if we plot the deviations from the mixture law against the fractional composition of the system. A very sharp maximum in this deviation curve will generally denote a small amount of

dissociation, whereas a flat curve will indicate that the compound is considerably dissociated.

In order to test these conclusions I have taken a hypothetical case of combination in solution and calculated the amounts of the different substances in the mixture by assigning arbitrary values to n and K.

If $n = 1$, *i.e.*, we have the reaction—

$$A + B \rightleftarrows AB,$$

and if $K = 0{\cdot}25$, we obtain the following numbers :—

y.	Mols AB x.	Mols free A $y - x$.	Mols free B $(1 - y - x)$.	Total Mols $(1 - x)$	Active Mass AB.	Active Mass A.	Active Mass B.
0	0	·000	1·000	1·000	0	0	1·000
·1	·078	·022	·822	·922	·085	·024	·891
·2	·151	·049	·649	·849	·178	·058	·764
·25	·182	·068	·568	·818	·223	·083	·694
·4	·259	·141	·341	·741	·349	·191	·460
·5	·276	·224	·224	·724	·382	·309	·309
·6	·259	·341	·141	·741	·349	·460	·191
·75	·182	·568	·068	·818	·223	·694	·083
·8	·151	·649	·049	·849	·178	·764	·058
·9	·078	·822	·022	·922	·085	·891	·024
1·0	0	1·000	0	1·000	·0	1·000	0

These numbers are plotted in Fig. 3. They show clearly the maximum in both number of mols and active mass of the compound AB when the composition of the whole system is 50 molar per cent. of A. The active mass being $\frac{x}{1 - nx}$, it must, of course, reach a maximum when x has a maximum value.

In Fig. 4 the results of the foregoing calculation are plotted somewhat differently. There the number of mols of B per 1 mol of A is represented along the abscissa, whereas the ordinates show as before the number of mols and the active mass of the compound. In this case x becomes unity only when the number of mols of B is infinitely great, and there is thus no maximum in the x curve. The active mass of AB shows, however, a maximum when $n = 1$, *i.e.*, again when the composition of the system is the same as that of the compound. Plotting the results in this manner shows clearly a fact which is often overlooked, viz., that although we are adding excess of B, *i.e.*, one of the products of dissociation of AB, still the active mass of the compound formed does not go on increasing continually, but soon reaches a maximum, owing to the dilution of the system by the excess of B. The position of this maximum, as already pointed out, depends only on the formula of the compound. It is interesting to note the form of the curve showing the variation in the amount of compound as the number of mols of B per 1 mol of A increases. It reminds one of the well-known curve expressing the relationship between the heat evolution and the number of mols of water per 1 mol of SO_3 or H_2SO_4. The type of curve remains the same, but undergoes a slight change in form according to the value of K. This is shown in Fig. 4, where x is plotted for $K = 0{\cdot}25$ and $K = 0{\cdot}01$. In the latter case the compound formed is almost undissociated, and the maximum in the active mass curve is very sharp.

Having obtained the amounts of each molecular species in solution, we can

construct property-composition curves as before. Assigning the arbitrary values for any (molecular) physical property,

$$A = 2,\ B = 1,\ AB = 0{\cdot}1,\ 1{\cdot}0,\ 2{\cdot}0,\ 4{\cdot}0,\ 6{\cdot}0,$$

we obtain the following values for the property of the different mixtures (S)—

y Mols A.	x No. Mols AB.	S Property of Mixture.	S^1 Property calculated on Simple Mixture Law.	$S^1 - S$ Deviation from Mixture Law.	$\frac{x}{S^1 - S} = p$	S_3 Value of Property for AB.
0	0	1·000	1·000	0	—	
·2	·151	·762	1·200	·438	·345	
·4	·259	·649	1·400	·751	·345	0·1
·5	·276	·700	1·500	·800	·345	
·6	·259	·849	1·600	·751	·345	
·8	·151	1·362	1·800	·438	·345	
1·0	0	2·000	2·000	0	—	

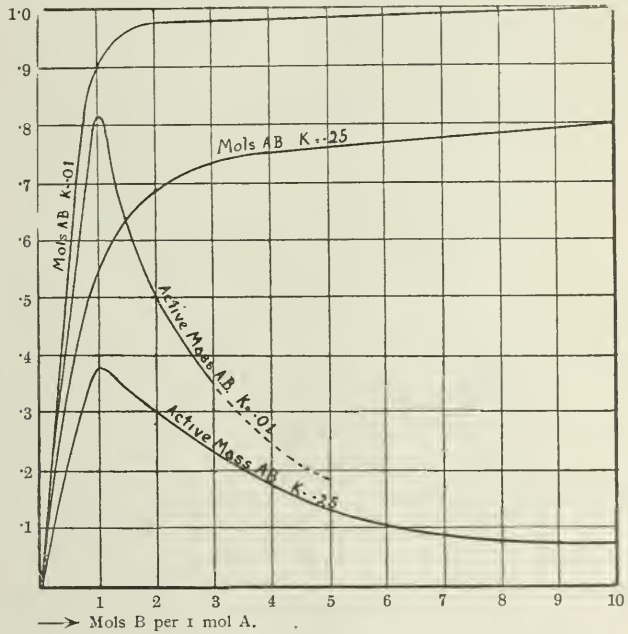


FIG. 4.

The values of S for the above values of S_3 (·1, 1·0, 2·0, &c.) give the property-composition curves shown in Fig. 5.

It is evident that all possible types of curve can be obtained by giving S_3 suitable values. There is thus no certain relationship between a given type of property-composition curve and the process of chemical combination in the mixture.

All that can be said with certainty is that a curve showing a pronounced maximum or minimum is more probably due to chemical combination than to any other process, owing to the fact that the active mass of the compound must pass through a maximum. It is not, however, by any means impossible

for a sagged curve to represent the result of chemical union between the components of the mixture.

The important curve is not, however, the property-composition, but the deviation curve. By a deviation curve is meant, of course, a curve expressing the deviation from the straight line plotted against the composition of the mixture. According to our theory, this curve must show a maximum when the fractional composition of the mixture is the same as that of the compound formed, *i.e.*, in our particular case at $y = \frac{1}{2}$.

The position of the maximum should be quite independent of everything else, *e.g.*, independent of K and of S_3. This is seen to be the case in Fig. 5, where the calculated deviation curves are plotted. Further, it is evident that if the

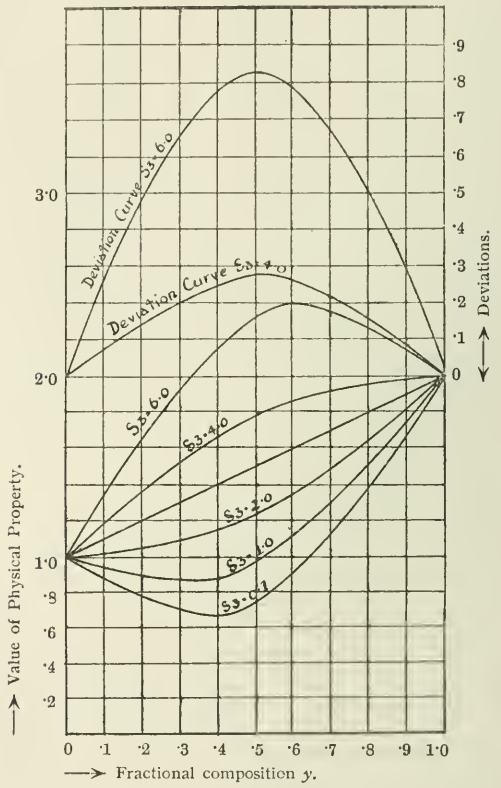


FIG. 5.

compound formed consists of one molecule of each component, the deviation curve must be symmetrical. If the compound contains a different number of molecules of A and B, however, this is no longer the case.

In the manner already indicated, by putting the measured deviation from the straight line proportional to the number of mols of compound formed, we can, by applying the principle of mass action, determine the equilibrium constant for the reaction, since the formula of the compound is given by the deviation curve alone.

The Influence of Temperature Change on Property-composition Curves.— It was mentioned earlier in the present paper that numerous observers

had noticed that when the property-composition curve exhibits a maximum the position of this maximum often moves along the composition axis with change of temperature. This movement is often very slight, but on the other hand it is sometimes relatively large. It was also pointed out that this phenomenon was one of the causes which lead chemists to be extremely sceptical with regard to the possibility of deducing chemical combination from property-composition curves. From what has been already stated, it is evident that the actual form of property-composition curve for a pseudo-binary mixture (*i.e.*, a binary mixture in which a third molecular species has been produced) depends on the relative amounts of the three kinds of molecules present, and also on their separate properties. Now change of temperature will, in general, alter K, that is, alter the relative amounts of the three substances present, although it does not alter the total fractional composition of the mixture (*i.e.*, the value of *y*). Moreover, each kind of molecule will have its own particular temperature coefficient for any physical property,

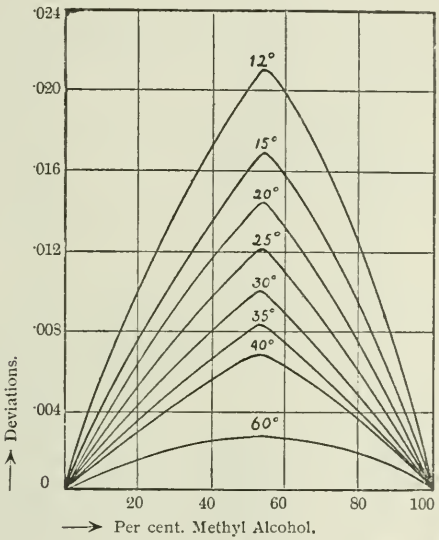


FIG. 6.—Deviations of Viscosity of Methylalcohol-Water Mixtures from Law of Mixtures at Different Temperatures.

Maximum deviation at 53 per cent. CH_3OH. $2CH_3OH \cdot 3H_2O = 54$ per cent.

and it is thus only to be expected that temperature change will alter the curve and so shift the position of the maximum.

It is, however, quite different with regard to the deviation curve. The deviation from the straight line we have seen to be proportional to the amount of compound in solution. The deviation must always reach a maximum when the concentration of the compound is a maximum, and this happens when $y = \frac{1}{n+1}$. This expression is quite independent of K, that is, of the relative amount of dissociation, and also independent of the value of the properties of the components and of the compound. The position of the deviation maximum must then be independent of temperature change. Whether the actual property-composition curve alters with temperature is, of course, quite immaterial to our method of arriving at the formula of the compound in solution. This should remove the difficulty already mentioned.

A confirmation of the above deductions is seen in Fig. 6, which represents the deviations from the straight line of the viscosity-composition curves for methylalcohol-water mixtures. The numbers are due to Petman.*

The figure shows very well the gradual approach of the deviation curve to a straight line as the temperature is raised. This indicates a diminishing amount of compound in solution at the higher temperatures. The compound must thus be formed with heat evolution. As is well known, the mixing of alcohol and water generates a considerable amount of heat. The results obtained in the present investigation may be briefly summarised as follows :—

1. A maximum or minimum in the property-composition curve of a binary mixture may be taken as giving possible indication of the formation of a chemical compound, although there is no certainty.

2. Sagged curves may be caused by dissociation or by chemical combination.

3. A process of increasing association in the mixture is unlikely.

4. Assuming that the straight-line law holds for mixtures in which the components undergo no molecular change on mixing, then the deviation from the straight line is proportional to the amount of new substance formed, and always reaches a maximum when the concentration of this new substance attains a maximum value.

5. If the new substance formed is a chemical compound, the concentration thereof is always a maximum when the mixture as a whole has the same fractional composition as the compound.

6. It is thus possible to determine the formula of the compound in solution and the degree of dissociation or the equilibrium constant for the formation of the new molecular species, from the deviation from the straight-line mixture law.

7. Although temperature changes may affect the form of the property-composition curve, especially as regards the position of a maximum therein, the position of the deviation maximum is independent of temperature changes.

8. Equilibria in homogeneous solution can thus be completely solved from physical determinations alone.

I should like to take the opportunity of apologising to any investigators in this field whose work I have omitted to mention. The reason is that I am placed in a position where no scientific library is at present available, and the only chemical journals at my disposal are a few copies of the *Journal* of the Chemical Society.

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* *Z. Chem. Phys.*, **4**, 486 (1906).

CONTRIBUTIONS TO THE KNOWLEDGE OF LIQUID MIXTURES—II.

CHEMICAL COMBINATION IN LIQUID BINARY MIXTURES AS DETERMINED BY A STUDY OF PROPERTY-COMPOSITION CURVES.

By ROBERT BECKETT DENISON, M.A., D.Sc., Ph.D.

(*A Paper read before the Faraday Society, Tuesday, March 26, 1912, Mr. Alexander Siemens, Vice-President, in the Chair.*)

In a previous paper I have indicated that a combination of the mixture law with the principle of mass action enables us to solve problems in homo-

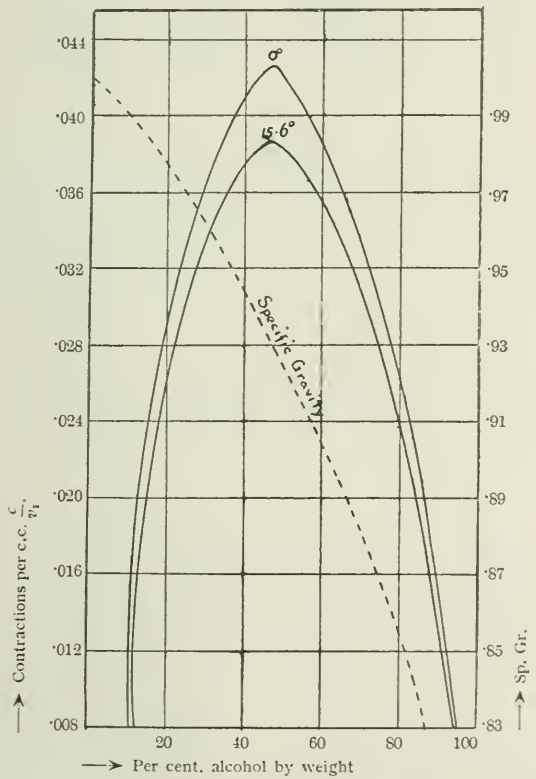

Fig. 1.—Contractions on mixing Ethylalcohol-Water at 0° and 15·6°.

geneous equilibria from a knowledge of physical data alone. It was shown that the actual form of the curve obtained by plotting physical property

against the composition of the mixture was of little value as a means of indicating the process taking place on mixing two liquids. The deviations from the mixture law are, however, very important. From them we can deduce the formula of the compound in solution, and if sufficiently accurate data are available the dissociation constant may be evaluated.

Table I.

Ethylalcohol-Water at 15·6°.

Per cent. Alcohol by Weight. w.	Sp. Gr. of Mixture. s_1.	Vol. before Mixing. v_0.	Vol. after Mixing. v_1.	Contraction. $c = v_0 - v_1$.	Contraction per c.c. $\frac{c}{v_1}$.
		c.c	c.c.	c.c.	
0	1·000	—	—	—	—
10	0·9841	102·598	101·616	0·982	0·0097
20	·9716	105·196	102·923	2·273	·0221
30	·9578	107·794	104·406	3·388	·0324
40	·9396	110·390	106·428	3·962	·0372
45	·9292	111·689	107·620	4·069	·0378
50	·9184	112·988	108·885	4·103	·0377
60	·8956	115·586	111·657	3·929	·0352
80	·8483	120·781	117·883	2·898	·0245
100	·7938 = s	—	—	—	—

In the following pages I intend to apply the principles already developed. Tables I. and II. contain the contractions which take place when 100 grams of a mixture is made up of different proportions of ethylalcohol and water at different temperatures. The last column contains the actual contractions

Table II.

Ethylalcohol-Water at 0°.

w.	s_1.	v_0.	v_1.	c.	$\frac{c}{v_1}$.
20	0·97566	104·806	102·495	2·311	0·0226
30	·96540	107·209	103·584	3·625	·0350
40	·94939	109·612	105·331	4·281	·0406
50	·92940	112·015	107·596	4·419	·0411
60	·90742	114·419	110·203	4·216	·0382

divided by the volume of the mixture. The resulting figures are proportional to the concentration of the compound formed. In Fig. 1 the values of $\frac{c}{v_1}$ are plotted against the fractional composition of the mixture. The specific-gravity curve for one temperature is also given. The same for the other temperature is practically parallel to it.

It is seen that the value of $\frac{c}{v_1}$ reaches a sharp maximum at 46 per cent. alcohol. According to the theory already given this composition must be that of the compound formed—

$$C_2H_5OH \,.\, 3H_2O = 46 \text{ per cent. alcohol.}$$

TABLE III.

Viscosity Deviations from Mixture Law—Ethylalcohol-Water Mixtures.

Per Cent. Alcohol by Weight.	η_0 Measured Viscosity.	η_1 Calculated from Mixture Law.	Difference $\delta = \eta_0 - \eta_1$.	
0	0·00891	·00891	—	
16	·01552	·00927	0·00625	
32·4	·02162	·00963	·01199	
46·2	·02368	·00994	·01374	
47·7	·02354	·00997	·01357	
50·2	·02337	·01003	·01334	Max. δ at 46
57·5	·02247	·01019	·01228	per cent.
61·1	·02212	·01027	·01185	alcohol.
70·5	·01995	·01048	·00947	
80·2	·01744	·01070	·00674	
100·	·01114	·01114	—	

TABLE IV.

Pyridine-Water Mixtures at 25°—Contractions on Mixing.

w.	s_1.	v_0.	v_1.	c.	$\frac{c}{v_1}$.
0	1·000	—	—	—	—
19·28	1·00117	100·450	99·883	0·567	·00568
29·99	1·00234	100·700	99·767	·933	·00935
49·57	1·00347	101·157	99·654	1·503	·01507
59·70	1·00297	101·393	99·704	1·689	·0169
70·34	1·00126	101·641	99·875	1·766	·0177
80·15	0·99694	101·870	100·307	1·563	·0156
90·08	·98870	102·102	101·131	0·971	·0098
100·	·9772	—	—	—	—

TABLE V.

Pyridine-Water Mixtures at 25°—Viscosity Deviations from Law of Mixtures.

w.	η_0.	η_1.	δ.
39·84	0·01833	0·00888	0·00945
59·7	·02187	·00887	·01300
66·7	·02225	·00887	·01338
70·3	·02186	·00886	·01300
80·1	·01894	·00886	·01008

It will be observed that the position of the maximum is exactly the same at 0° and 15·6°. This fact, too, is predicted by theory. The sharpness of the

maximum is greater at the lower temperature, indicating a dissociation of the compound with rise of temperature. The formation of the compound must hence be exothermic. It is, of course, true that alcohol and water generate heat on being mixed.

The deviations from the straight line of the viscosity curve for the same system are shown in Table III. and plotted in Fig. 2. Again we have a sharp maximum at 46 per cent. alcohol, indicating the formation of the same compound. In this case the actual viscosity curve also has a maximum point at almost the same composition of the mixture. This is due, however, to special circumstances, namely, that the viscosity of the compound is very much greater than that of the two components. In this case the straight line joining the values of the viscosity of alcohol and water respectively becomes

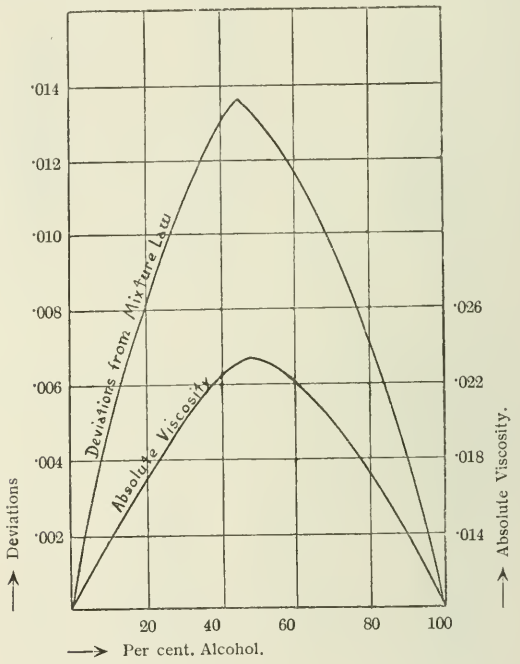

Fig. 2.—Ethylalcohol-Water Viscosity Deviations.

relatively almost parallel to the composition axis. The point of maximum deviation must in such cases practically coincide with the position of the maximum in the property-composition curve.* It is only in cases like this that the actual property-composition curves give direct evidence of the formation and the formula of a compound in solution.

Another mixture for which accurate data are available is that of pyridine-water. This system has been excellently studied by Hartley, Thomas, and Appleby.† Here both specific-gravity and viscosity curves go through a maximum. At 25° the positions of the respective maxima are at 18 and 32 molar per cent. pyridine. If one attempted to deduce the formulæ of compounds in solution from these curves one would obtain a different formula from each of the curves. Plotting the contractions on mixing and the

* See Fig. 5 in the previous paper.

† *J.C.S.*, March, 1908, 545.

viscosity deviations, we obtain in each case a maximum deviation at 68 per cent. pyridine—

$$C_5H_5N \,.\, 2H_2O = 68{\cdot}6 \text{ per cent. pyridine.}$$

Details are given in Tables IV. and V. and the results are plotted in Fig. 3.

Hartley also plots the viscosity of $\frac{N}{8}$ lithium nitrate in pyridine-water mixtures, and finds that the composition at which the maximum viscosity occurs is quite unaltered by the presence of the salt. This is precisely what our theory would predict. The viscosities of pyridine and water are very

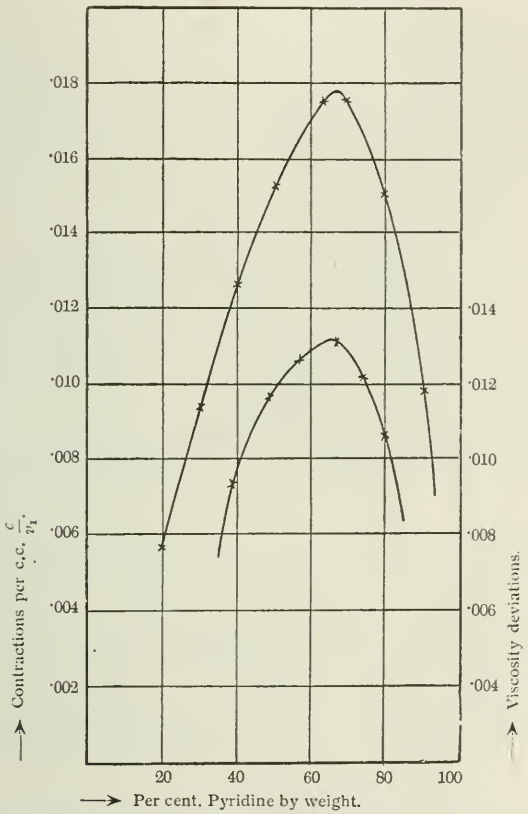

FIG. 3.—Pyridine-Water Contractions on Mixing and Viscosity Deviations at 25°.

nearly equal, and consequently the position of maximum viscosity practically coincides with that of maximum deviation. Now the position of the latter depends solely upon the formula of the compound in solution, and this is not likely to be affected by a dilute solution of lithium nitrate. It might, however, be very different if large amounts of some strongly hygroscopic salt were added. The pyridine-water complex would then probably break down into a simpler one or into pyridine and water. This would be immediately shown by a great change in the position of the maximum deviation, viz., from 33 to 50 molar per cent. pyridine ($C_5H_5N \,.\, H_2O$), or the deviations would become practically zero and the straight-line law be obeyed (no compound formed).

« Picoline-water mixtures according to Dunstan* give a maximum viscosity at a composition of 67 per cent. picoline. The specific-gravity curve shows no maximum. Both contraction on mixing and viscosity deviation reach a maximum at about 64 per cent. picoline. The position of these maxima is not too certain, owing to the small number of determinations. The trihydrate requires 63·2 per cent. picoline.

The viscosity curve for lactic acid-water mixtures † shows no maximum. It is a typical sagged curve, always below the theoretical straight line. Dun-

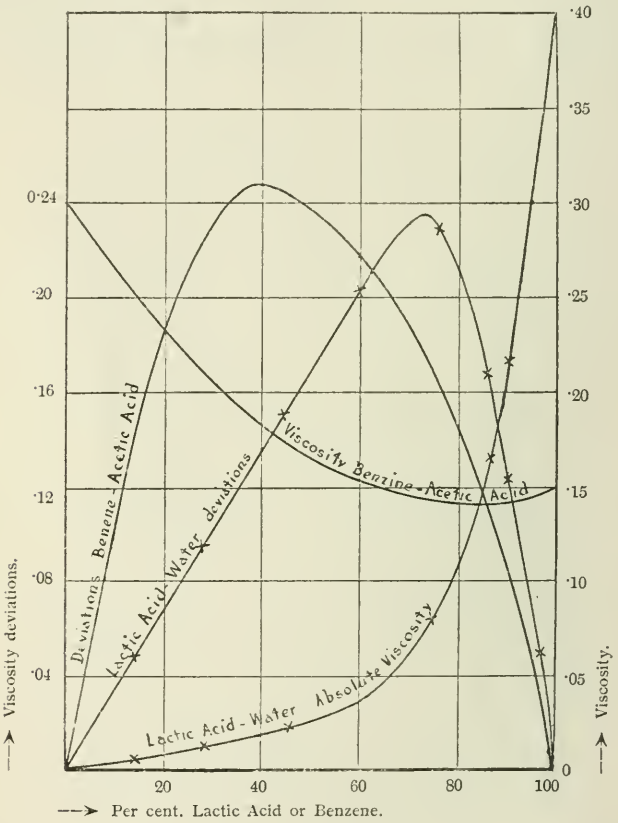

FIG. 4.—Viscosity and Viscosity Deviations for Lactic Acid-Water and Benzene-Acetic Acid.

stan attributes the form of the curve to a process of molecular dissociation. This might be possible, but there are other grounds for believing that lactic acid unites with water. In the case of a curve like the present one (see Fig. 4), which might theoretically be due to dissociation or to chemical combination, we have the following method of deciding the question :—

If the deviation curve reaches a maximum at a composition of the system expressing a simple molecular relationship between the two components, then we must take chemical combination as being the cause of the sagging in the property-composition curve. If not, then molecular dissociation takes place.

* *J.C.S.*, October, 1907, 1731. † Dunstan, *J.C.S.*, January, 1905, 14.

If the components mix with evolution of heat, chemical combination is again most likely. At higher temperatures the deviation from the straight line would become less if due to chemical union, but should increase if due to dissociation.

In the example before us the deviation curve exhibits a sharp maximum at 72 per cent. lactic acid—

$$C_3H_6O_3 . 2H_2O = 71{\cdot}5 \text{ per cent.}$$

In this case the compound has a much less viscosity than the lactic acid itself.

Benzene-acetic acid mixtures* give a viscosity curve with a somewhat faint minimum. Dunstan attributes this to a dissociation of acetic acid molecules, although he mentions that the position of the minimum corresponds approximately to a composition $5C_6H_6 . C_2H_4O_2$. The curve is somewhat like a possible property-composition curve where dissociation of one of the components occurs. The corresponding deviation curve, however, exhibits a very pronounced maximum at 39–40 per cent. benzene—

$$C_6H_6 . 2C_2H_4O_2 = 39{\cdot}4 \text{ per cent.}$$

Again, acetone-ethylalcohol mixtures give a sharp maximum viscosity deviation at 38·5 per cent. acetone, $C_3H_6O . 2C_2H_6O = 38{\cdot}6$ per cent. Many other cases might be quoted, but it would seem that sufficient evidence has been brought forward to justify the deduction of the formulæ of components in solution by means of a study of the physical properties of mixtures.

The Evaluation of the Dissociation Constant of a Compound in Solution.—If we have a system composed of y mols total A and $(1 - y)$ mols total B and x mols of a compound AB_n are formed, then the equilibrium is governed by the relationship—

$$(y - x)(1 - y - nx)^n = KV^n x,$$

if active mass be taken as mols per unit volume, or

$$(y - x)(1 - y - nx)^n = Kx\,(1 - nx)^n,$$

if we put the active mass equal to the fraction of the total number of mols present.

Since the deviation from the straight line (δ) is proportional to the number of mols of compound formed, we have—

$$x = p\delta.$$

Substituting for x we obtain—

$$(y - p\delta)(1 - y - np\delta)^n = Kp\delta V_1^n,$$

and for another value of y—

$$(y_1 - p\delta_1)(1 - y_1 - np\delta_1)^n = Kp\delta_1 V_1^n.$$

In these equations everything is known except p and K. By eliminating the one we obtain, of course, the value of the other.

If n is greater than 1, as is usually the case, the solving of these equations is very laborious. I have been unable to find accurate numbers for a binary mixture with chemical combination where $n = 1$. By extending the

* Dunstan, *loc. cit.*

principle of this paper we can, however, test the results by some accurate data in regard to electrolytes.

The volume changes which occur on mixing liquids have been studied by Holmes * and Sageman.† These authors attribute such changes to purely physical molecular processes on mixing. They come to the conclusion that chemical combination in solution is unnecessary to explain the deviations of binary mixtures from the simple mixture law, and they point out that their interpretation of the facts is totally incompatible with any "hydrate" theory of solution. Furthermore, their theory leads them to the remarkable conclusion that there is no chemical combination, *i.e.*, no formation of bisulphate when sulphuric acid and normal sulphate are mixed in aqueous solution. This conclusion is difficult to reconcile with the fact that bisulphates can be obtained from the solution, since a substance cannot crystallise from a solution which does not contain it. The actual amount in solution, it is true, may be small, but it must be finite. However, the electrolysis of bisulphate solutions would appear to show that the amount of bisulphate present as such is considerable. I propose to show that the accurate experimental figures of the above authors afford excellent quantitative evidence of the formation of bisulphate if viewed from the standpoint of mass action. Incidentally they serve as a test of the theory put forward by the present author.

Let us assume, then, that the formation of bisulphate takes place on mixing solutions of H_2SO_4 and K_2SO_4 according to the equation—

$$H_2SO_4 + K_2SO_4 \rightleftarrows 2KHSO_4.$$

Neglecting ionisation (which makes but little difference in the present case) and considering only un-ionised molecules, let us further suppose that in a mixture of y mols K_2SO_4 and $(1-y)$ mols H_2SO_4 there are formed $2x$ mols $KHSO_4$.

The system then consists of—

$$\left.\begin{array}{rll} (y-x) & \text{mols free} & K_2SO_4 \\ (1-y-x) & \text{,,} \quad\ \text{,,} & H_2SO_4 \\ 2x & \text{,,} \quad\ \text{,,} & KHSO_4 \end{array}\right\} \text{total 1.}$$

Hence according to the law of mass action we have—

$$(y-x)(1-y-x) = Kx^2.$$

Owing to the fact that there are equal numbers of mols on each side of the equation, the volume of the system has, of course, no effect on the equilibrium.

Differentiating with respect to y, we find that the number of mols and the active mass of bisulphate in the system is a maximum when $y = \frac{1}{2}$, *i.e.*, when the system as a whole contains equal molecular amounts of the two components.

But on our theory x is proportional to the contraction on mixing, and hence this contraction should reach a maximum value at the composition $y = \frac{1}{2}$. It is evident from the curves shown in Fig. 5 (taken from Holmes's paper) that this is very exactly the case.

From the equation $(y-x)(1-y-x) = Kx^2$ we see that when K approaches zero, *i.e.*, total combination between the components, $(y-x)(1-y-x) = 0$.

The relation between x and y is then represented by two straight lines

* *J.C.S. Trans.*, 1906, 89, 1774. † Ibid., 1907, 91, 1606.

equally inclined to the composition axis and meeting at a point whose abscissa is given by $y = \frac{1}{2}$. This is exactly the case given by Holmes for solutions of HCl and NaOH, where combination is, of course, practically complete. When combination is not complete, *i.e.*, the compound formed is more or less dissociated, the straight lines become curves, and instead of a point maximum where two straight lines meet, we get a smooth curve with a more or less pronounced maximum. Hence the flattening of the curve at the maximum must give a rough measure of the stability of the compound formed. But the relative stability of a series of acid salts in the presence of excess of water should be proportional to the "strength" of the different bases. Hence the order of stability of the bisulphates should be $KHSO_4$, $NaHSO_4$, NH_4HSO_4,

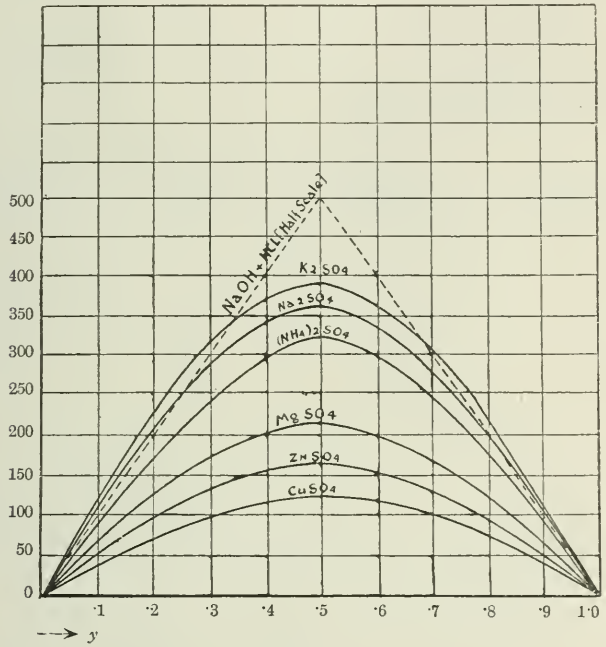

Fig. 5.

$Mg(HSO_4)_2$, $Zn(HSO_4)_2$, $Cu(HSO_4)_2$. It will be observed that this is precisely the order of stability as deduced from the curves given by Holmes and Sageman (see Fig. 5).

Putting the number of mols of bisulphate proportional to the expansion on mixing we have—

$$r = p\delta,$$

and substituting in the mass action equation for x we obtain—

for $y = 0{\cdot}25$—

$$(0{\cdot}25 - 0{\cdot}269p)\,(0{\cdot}75 - 0{\cdot}269p) = K \times (0{\cdot}269)^2 p^2\,;$$

for $y = 0{\cdot}5$—

$$(0{\cdot}5 - 0{\cdot}394p)\,(0{\cdot}5 - 0{\cdot}394p) = K \times (0{\cdot}394)^2 p^2.$$

From these two equations $p = 0{\cdot}82$.

Similarly the experimental expansions for other values of y can be used to obtain a value of p. Were there no experimental errors p would always have

the same value. The value of p as deduced from all the measurements given for the system under consideration is not quite constant, but very nearly so. The mean value of p is very near—

$$p = 0{\cdot}80.$$

Substituting for p we obtain the following values for K—

$y = 0{\cdot}2$	0·25	0·33	0·5	0·67	0·75
$K = 0{\cdot}29$	0·40	0·34	0·34	0·32	0·29

Mean $K = 0{\cdot}33$.

When one considers the cumulative effect of any experimental error on the value of K the constancy attained above is quite satisfactory. It shows that the process causing the expansion on mixing, whatever its nature, is governed by the law of mass action in the form set down.

Taking the mean value of K and recalculating x for the different mixtures we obtain the following numbers :—

Fraction Mols K_2SO_4 in the Mixture. y.	Fraction Mols $KHSO_4$. x.	Calculated Expansion $= x$ Multiplied by $\frac{39400}{316}$.	Holmes's Experimental Value for the Expansion on Mixing.
0·2	0·182	227	230
0·25	·220	274	269
0·33	·270	337	338
0·50	·316	394	394
0·67	·271	340	340

The numbers in column 3 are the values of the amount of bisulphate in solution multiplied by a constant so as to convert one of them into the actual experimental expansions given by Holmes and Sageman. If the formation of bisulphate can account for the volume changes on mixing, these calculated expansions should agree with the experimental ones. It is evident that the agreement is an excellent one.

These calculations show, moreover, that the theory of binary mixtures developed by the author of the present paper is applicable to the investigation of equilibria in ternary liquid systems when one component is in large excess. The method of evaluating p and x given above may become rather laborious, and, moreover, needs very accurate experimental data in order to give anything like constant values for p. A much shorter, but somewhat less accurate, method of obtaining the same result is given below.

From the mass action equation $(y - x)(1 - y - x) = Kx^2$ we have seen that when chemical combination is practically complete the relation between x and y is given by two straight lines equally inclined to the axes. These straight lines, meeting at the point $y = \frac{1}{2}$, $x = \frac{1}{2}$, are the tangents to the extremities of the deviation curve, *i.e.*, tangents at the points $y = 0$ and $y = 1$. If chemical combination is not complete, then the curve giving the relation between x and y has a maximum at $y = \frac{1}{2}$, but the corresponding x value is less than one-half. Since the deviation is proportional to x we have the relationship—

$$\frac{\text{actual value of } x}{\frac{1}{2}} = \frac{\text{actual distance of maximum in deviation curve above } y \text{ axis}}{\text{actual distance of point where tangents meet above } y \text{ axis } (y = \frac{1}{2})}$$

By plotting the experimental expansions for the system $K_2SO_4 - H_2SO_4$ on a large scale, it is found that the tangents to the curve at the points $y = 0$ and $y = 1$ meet at a point $x = 630$, when the maximum experimental expansion is 394. There is, of course, a considerable degree of uncertainty in the estimation of this point, hence the probable inaccuracy of the result.

In the case before us we see, then, that if combination were complete ($x_1 = \frac{1}{2}$), the measured expansion would be 630 units. Hence—

$$\frac{x}{\frac{1}{2}} = \frac{394}{630}$$
$$x = 0{\cdot}313$$
$$p = 0{\cdot}79$$

The values previously obtained by solving the separate equations for p and x were $x = {\cdot}316$, $p = {\cdot}80$.

The agreement in this case is much better than is likely to be obtained as a general rule. It shows that in any case this geometrical method of evaluating x and K gives at least approximately correct results.

According to the principles expressed in the present theory it is apparently necessary that the deviation curve for a given mixture shall pass through its maximum at the same composition of the system whatever be the particular physical property under consideration. With regard to the two properties considered in this paper, viz., specific volume and viscosity, this has been found to be the case.

It would appear possible, however, that exceptional cases might be discovered, and the following forecast of such cases may be not without interest.

If we can represent the value of any (molecular) physical property of a binary mixture in which chemical combination has taken place by the relation—

$$s = (y - x)\, s_1 + (1 - y - nx)\, s_2 + x s_3,$$

where—

s = the value of the property of the mixture,

s_1, s_2, s_3 = the value of the property of the components and the compound respectively,

y = the total molar fraction of the first component present (A),

and—

x = the number of molecules of compound ABn formed.

Then, if $x = 0$, the simple mixture law would hold good and the property of the mixture would be given by—

$$s^1 = y s_1 + (1 - y) s_2.$$

Hence the deviation from the straight line—

$$s^1 - s = x s_1 + n x s_2 - x s_3 = x [s_1 + n s_2 - s_3].$$

If now by chance $s_3 = s_1 + n s_2$, the simple mixture law will be obeyed, even if chemical combination has taken place.

There is always, therefore, the possibility that for a given physical property the deviations from the simple mixture law may be less than the experimental error, even when chemical combination has taken place. If, however, any other physical property be considered, it is almost inconceivable that a similar relationship should hold. Hence, with most other physical properties a well-defined maximum deviation should be observed.

Further, the case seems possible where the same mixture might give a deviation maximum with regard to specific volume at one composition and a maximum viscosity deviation at a widely different composition.

Suppose the compound formed in solution is almost undissociated, *i.e.*, K has a very small value. At the point of maximum concentration of compound the system then consists of practically pure compound. It is then possible, in fact in some cases highly probable, that on further addition of the second component B, a new compound may begin to be formed in finite quantity, the first component A having practically disappeared from the system.

If we denote the two compounds by AB and AB_2, it is quite possible that AB may differ but slightly from A and B in specific volume, but largely in viscosity. On the other hand, AB_2 may have a specific volume widely different from AB, but a viscosity of almost the same value. In this case the specific volume deviation curve would show a maximum at 33·3, and the viscosity deviation curve a maximum at 50 molar per cent. A. Both maxima would thus occur at compositions representing definite compounds. Cases of this nature are only to be expected when the chemical affinity between the two components of the mixture is very great.

Such cases as the one just mentioned, where combination between the components takes place to a very considerable degree, are very interesting. As we have seen, on one side of the point of maximum concentration of compound we have a solution of compound in the component A, and on the other side one of compound in component B. The two solutions are thus quite distinct and may have very different properties. As far as the author's knowledge goes, the only extended observations bearing on this point are those of Gibson.* He finds that solutions of the strong acids have very different properties according as the composition is weaker or more concentrated than that corresponding to maximum specific electrical conductivity.

To take an example, it has been observed that if a few drops of hydrochloric acid be added to saturated solutions of KCl, NaCl, NH_4Cl, or RbCl, precipitation of the chloride takes place in all cases if the concentration of the added acid be greater than that corresponding to maximum conductivity. If the acid be of less concentration there is no precipitation in any case. These facts are unexplainable on the ionic theory, but are easily accounted for on Gibson's theory that such systems have a tendency towards maximum conductivity.

On the present theory, the fact that solutions of hydrogen chloride do not conform to the law of mixtures would be accounted for by chemical union between HCl and water.

Now pure HCl and pure H_2O have practically the same electrical conductivity as compared with that of their mixtures. Hence the composition of the HCl-H_2O mixtures, corresponding to maximum conductivity, must be very near that corresponding to maximum concentration of hydrate.

Since the formation of hydrate is a process that takes place of itself, *i.e.*, with a decrease in the free energy of the system, the free energy of the system must be a minimum when the concentration of the hydrate is a maximum. That is, for all ordinary reactions in concentrated aqueous HCl solutions in which water takes part there will be a tendency for the system to run down to its lowest energy level, that is, to the point where the concentration of hydrate is a maximum. More concentrated HCl solutions will thus tend to abstract water from other aqueous solutions in order to form a

* *Trans. Royal Soc. Edin.*

solution with a greater concentration of hydrate. If these happen to be saturated with salt, then some salt must be precipitated unless the energy requirements are satisfied in some other way, *e.g.*, by combination between HCl and the salt. As a matter of fact experiments showed that the amount of NaCl precipitated is roughly equal to the calculated amount, on the assumption that the excess of anhydrous HCl in the system diluted itself until it just reached the concentration corresponding to maximum specific conductivity. On the other hand, a solution of HCl of less concentration than that corresponding to maximum concentration of hydrate will have no tendency to take up water, since by doing so it could only form a solution containing a smaller concentration of hydrate. Hence the addition of HCl of a concentration only slightly below that containing a maximum concentration of hydrate will be unable to abstract water from a saturated salt solution, and so cannot cause precipitation. These views are easily accommodated to the fundamental principles of the ionic theory.

A maximum specific conductivity means almost certainly a maximum concentration of conducting particles or ions. If combination with the solvent is a necessity for the ionisation of the strong halogen acids, which in the anhydrous state are non-conductors, then a maximum concentration of compound means a maximum concentration of ions, according to the relationship—

$$\text{Concentration of ionising body} = K\ [\text{concentration of ions}]^n.$$

In very dilute solutions, the concentration of compound is, of course, proportional to the concentration of dissolved substance, and it is immaterial whether the dissolved body is hydrated or not.

The theory of chemical union between solvent and dissolved substance, as has often been pointed out, is by no means in opposition to the ionic theory. In concentrated solutions of electrolytes, however, the un-ionised part of the solute will most probably play the predominant rôle. It is probable that any extension of the ionic theory so as to afford a quantitative survey of concentrated solutions must take place on some such lines as are suggested in this paper. To the author it would seem most probable that in many cases combination with the solvent must precede ionisation, and that hydration of the molecule is a much more important process than hydration of the ions. This does not, of course, preclude the possibility of some substances ionising without combination with the solvent. Many salts seem to be ionised to a small extent in the solid form, in which case, solution would naturally mean an increased degree of ionisation.

It is hoped to communicate in a future paper the results of measurements which are now in progress with the object of further testing the above theory in a quantitative manner.

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DISCUSSION.

Dr. C. H. Desch (*communicated*): The author's discussion of the criteria to be used in deciding as to the existence of compounds in binary liquid mixtures should be of great assistance to workers on solutions, and has the advantage of being independent of any theory as to the constitution of solutions. An application of the same method to properties other than viscosity

and specific volume should lead to further interesting results. The case of liquid alloys may be compared with that of aqueous solutions and is a peculiarly simple one, both solvent and solute being elementary substances. It has been shown * that the conductivity curve of molten sodium amalgams exhibits a strongly marked maximum at the composition corresponding with the compound $NaHg_2$, which is known to be formed with large development of heat. This case is a simple one, as the conductivity is purely metallic, electrolysis not occurring in alloys. The curve for liquid alloys of sodium and potassium shows a minimum, without any indication of a compound. However, by taking the actual measurements of this series † and plotting the deviations from the straight line, curves are obtained for each temperature, which show a maximum in the neighbourhood of the composition Na_2K, a compound which is known from thermal analysis to exist, although the number of points on Müller's curves is insufficient to fix the position of the maximum very accurately. As pointed out by the author, the position of a maximum on the deviation curve should be independent of temperature if due to the formation of a compound. It should also be unaffected by the addition of a third, chemically indifferent, substance to the solution. This method is of use in distinguishing two types of freezing-point curve, one with a maximum due to a compound, the other a curve of solid solutions presenting a maximum without chemical combination. The former, but not the latter, remains unchanged in position when a third substance is added to the fused mixtures, and it would seem probable that this method, which is applicable to solid solutions, should also be capable of being applied to binary liquid mixtures.

Professor Alfred W. Porter (*communicated*) : Mr. Denison's Paper contains an ingenious attempt to devise a more definite way of deciding upon possible association between mixed liquids. Any attempt in this direction ought to be encouraged, for in the absence of a definite theory, deviation of any property curve from a straight line is very slender evidence indeed on which to base the assumption of association. One or two remarks, however, seem to be called for in relation to this particular attempt. It is important to notice that Mr. Denison's method depends upon a particular mode of specifying the masses that come into play in connection with applications of the mass law. For two liquids in equilibrium with a supposed compound he first writes (p. 28)—

$$(y - x)(1 - y - nx)^n = KV^n x,$$

this being the usual form of writing the equilibrium equation. Owing to difficulties in regard to differentiation, he then replaces this by another equation involving instead so-called "active masses," viz.—

$$(y - x)(1 - y - nx)^n = Kx(1 - nx)^n.$$

Now this change is a perfectly arbitrary one, and it is necessary to point out that it is equivalent to overthrowing any theoretical basis upon which the law of mass action holds. To illustrate this, take the first example in his second paper—that of the contraction of ethylalcohol-water mixtures. The volume V which contains 1 gr. mol of both varies from 18 c.c. when the mixture is all water ($y = 0$) to about 58 c.c. when it is all alcohol ($y = 1$), and this variation occurs nearly in a linear way. On the other hand, the factor in the second equation which replaces V varies from zero and back to zero again in

* K. Bornemann and P. Müller, *Metallurgie*, 1910, **7**, 396.
† P. Müller, *Metallurgie*, 1910, **7**, 730, 755.

the same range. Since he concludes that association takes place with three molecules of water, the value of n is 3. Hence, in the first equation we have a factor varying from 1 to 25 nearly, while the factor which replaces it does not *on the whole* vary at all, and for intermediate concentrations is *less* than for the extremes. This illustration shows that Mr. Denison's method of measuring "masses" may lead to results widely at variance with those derived from the customary methods.

Since it must be admitted that the ordinary equations of equilibrium require modification for strong solutions (and at present the necessary modification is unknown), it cannot be declared that Mr. Denison's method is wrong; but it certainly requires more justification than the facility it introduces into an operation of differentiation.

It ought further to be borne in mind that when account is taken of molecular forces we have no right to expect a straight-line variation in the physical properties, even if no combination at all takes place between the constituents. Any derivation of the degree of association which does not take this fact into account is essentially misleading.

Dr. R. Beckett Denison (*communicated reply*): Professor Porter's criticism is directed chiefly against my representing the "active mass" of a constituent of a mixture by its molar fraction. This point of view may be somewhat unorthodox, and to attempt to justify it would really require the writing of another paper. At present I merely wish to point out that I have not adopted this conception of active mass simply and solely because it facilitates a mathematical process.

First of all, what is to be understood by the term "active mass"? This must depend upon one's definition of an ideal solution. If one takes the original van't Hoff definition that an ideal solution is one which obeys the relationship

$$pv = n\mathrm{RT}$$

where p is the osmotic pressure and v the volume of the solution, then we must express active mass as mols per unit volume. However, as Professor Porter points out, this relationship fails completely for concentrated solutions, and therefore especially for binary mixtures throughout their whole range of composition. Now I have defined my ideal binary mixture as one whose property-composition curve is a straight line. If any molecular property for such a mixture be plotted against the fractional molar composition, the resulting curve is a straight line.

Moreover, I regard the active mass of any constituent of a mixture as equivalent to the proportion of any attribute, physical or chemical, of the mixture which is directly contributed by that constituent.

This conception of active mass may or may not be correct, but at any rate, having defined my ideal solution as above, I am compelled to put active mass equivalent to molar fraction. If the deductions from this conception fit the facts, then the conception must have some value as a working basis.

As a matter of fact, the expression of active mass by the molar fraction is not employed in my paper for the first time. Whilst working on this matter, papers have appeared by G. N. Lewis * and by Dolezalek † who find that for binary mixtures in general the molar fraction conception of active mass gives better results than any other. Lewis gives a general thermodynamic theory of solution on this basis, and Dolezalek finds that in binary mixtures

* *Proc. Amer. Acad.*, **43**, 259, 1907; *Z. Phys. Chem.*, **61**, 129, 1907; *J. Amer. Chem. Soc.*, xxx., 668, 1908.

† *Z. Phys. Chem.*, lxiv., 727, 1908.

the partial vapour pressure of each constituent is proportional to its molar fraction throughout the whole range of composition.

This should be sufficient evidence to show that there is not much fear of the employment of molar fraction as representing active mass giving results, as Professor Porter says, widely at variance with those derived from the customary methods. There are no customary methods which yield satisfactory results for concentrated solutions. For gases and for dilute solutions where the ordinary van't Hoff's law holds good, then both conceptions of active mass yield identical results. Furthermore, the representation of active mass by molar fraction enables us to deduce certain well-known experimental relationships much more easily than by any other method. Compare, for example, the ordinary text-book proof of Raoult's law with the following :—

For a pure solvent in contact with vapour at constant temperature $\frac{C_{vap.}}{C_{liq.}} = K'$ by Nernst's distribution principle.

Putting $C_{liq.}$ equal to molar fraction $= 1$ and C_{vap} proportional to the vapour pressure of the pure solvent p_o, we have $p_o = K$.

Now, dissolve n mols non-volatile solute in N mols solvent. Again $\frac{C_{vap.}}{C_{liq.}} =$ constant, and since the active mass of the solvent is now $\frac{N}{n+N}$ we have—

$$\frac{p}{\frac{N}{N+n}} = K = p_o$$

Whence—

$$\frac{p_o - p}{p_o} = \frac{n}{N+n}$$

which in dilute solution becomes $\frac{n}{N}$.

With regard to Professor Porter's last remark *re* molecular forces, I must point out that a chemist regards such forces as quite subordinate to the forces of chemical combination, and that my paper deals chiefly with chemical combination in liquid mixtures. Furthermore, binary mixtures are undoubtedly known which obey the straight-line law within the limits of experimental error. Surely intermolecular forces must act in these cases ! It may or may not be the case that such forces affect the straight-line law, but the onus lies with the physicist to show that they do so to an extent outside the limits of experimental error.

In conclusion, I can only thank Professor Porter for his criticism. I have read it with great interest and replied to it in order to try and point out that my conceptions have a broader foundation than that of a mathematical trick. I think, however, there is one slight error in Professor Porter's remarks. The factor replacing v is $(1 - nx)$. As x varies from 0 to 0, this must vary of course from 1 to 1, and not from zero to zero as is inadvertently stated in the criticism.

Natal University College,
May 24, 1912.

ELECTROLYSIS IN LIQUEFIED SULPHUR DIOXIDE.

By L. S. BAGSTER, B.Sc., and B. D. STEELE, D.Sc.

(*A Paper read before the Faraday Society, Tuesday, March 26, 1912, Mr. Alexander Siemens, Vice-President, in the Chair.*)

Although considerable attention has been devoted in recent years to the study of the solvent properties of various inorganic and organic chemicals, most of the work that has been carried out has dealt only with the power possessed by various solvents to form conducting solutions and with the relation between this power and certain physical properties of the solvent. Of the large number of investigations of this character, reference may be made to the work of Franklin, Kraus, and others on liquefied ammonia, and especially to those of Walden and his collaborators on a very large number of solvents, both inorganic and organic, and to the investigations of the liquefied halogen hydrides by Steele, McIntosh, and Archibald.

The majority of the above-mentioned investigators have examined the conductivity of solutions in the various solvents, but the behaviour of these solutions during electrolysis has only been examined carefully in the case of solutions in ammonia.

The purpose of the present investigation was to extend our knowledge of some of the lesser-known inorganic solvents, and in particular to determine, if possible, the mechanism of electrolysis in solutions in these solvents. Liquefied sulphur dioxide has been selected as the most convenient solvent to use for two reasons. Firstly, that it is easily obtained in quantity and is liquid at the temperature of boiling ammonia; and secondly, that as a compound containing no hydrogen it should present the greatest possible contrast in its general behaviour to that of water.

The fact that minute traces of moisture profoundly modify the nature of the reaction has interfered with the rapid progress of the investigation, and considerable difficulty has been experienced throughout in carrying out the manipulations on account of the difficulty of excluding moisture.

Ultimately it was found necessary to carry out certain of the experiments *in vacuo* with very carefully dried apparatus and materials.

The electrolysis of the following substances when dissolved in liquefied sulphur dioxide has been investigated :—

(*a*) Potassium iodide and sodium iodide.
(*b*) Trimethylsulphonium iodide.
(*c*) Tetramethylammonium iodide.
(*d*) „ „ sulphate.
„ „ sulphite.
(*e*) Hydrogen bromide.
(*f*) Mixture of hydrogen bromide and either water or an organic compound.

Potassium Iodide and Sodium Iodide.

There appears to be no qualitative difference in the behaviour of these two substances when their solutions are electrolysed. A description of the behaviour of a solution of potassium iodide will therefore be sufficient.

Preliminary experiments were carried out in an apparatus consisting of two glass tubes about 1 cm. in diameter, which were joined together near the bottom by a somewhat narrower tube, the object of the latter being to minimise as far as possible the mixing of the cathode and anode solutions during the experiment.

It was soon found that the resistance of this system was variable and very high when small platinum electrodes were used. When the circuit was first closed, the current, which started at about 200 milliamperes, fell very rapidly to the value of about 1 milliampere. On reversing the current, it rose momentarily to the value of about 40 milliamperes, and again fell very rapidly to about 1 milliampere. On again reversing, the current rose, but never to its original high value. If this process of reversal was repeated a great number of times, it was found that after each reversal the maximum value to which the current rose became less and less, until finally practically no current passed at all at the original potential difference. If the latter was raised considerably, the resistance, which appeared to have been gradually built up, broke down, and the same behaviour could then be repeated at the new voltage. On substituting a fresh pair of platinum-wire electrodes the same behaviour could be repeated, thus indicating that the very high resistance was located at the surface of the electrodes. The cathode at the close of such an experiment was found to be coated with a minutely crystalline dark-coloured deposit, which, as the liquefied SO_2 evaporated, became white in colour.

The gradual cutting off of the current is therefore accompanied by the formation of a deposit on the cathode.

At the anode no changes were observed, but the changes which can occur during this experiment are of such a small magnitude, on account of the cutting off of the current, that in all probability iodine, if liberated at the anode, could not be detected.

When an e.m.f. of 40 to 80 volts is applied to the electrodes, it sometimes happens that if the current flowing is large for the first few seconds, gas appears to be evolved at both electrodes, and as long as this happens the current is erratic, but does not fall to the low value which it reaches when no gas is formed.

With larger platinum electrodes of about 1 to 3 cm. area, the changes are very similar, with the difference which might be anticipated that it takes longer for the current to fall from its initial high to its extremely low value, and that iodine is liberated at the anode and forms there a characteristic red solution in the sulphur dioxide. There is, moreover, little or no evidence of gas evolution.

When mercury electrodes were substituted for platinum, it was found that the general behaviour was the same as before. In this case, however, stirring the liquid electrode caused a rise in value of the current, and at the anode a green compound was formed as a scum on the surface of the mercury. This green substance was probably mercurous iodide.

Experiments with silver and copper cathodes showed that with these the current did not exhibit any of the erratic variations which were found with Pt and Hg cathodes ; the silver (or copper) became covered with a dark brown, almost black, deposit, in all probability silver (or copper) sulphide

which, since it is a conducting substance, does not cut off the current. Iodine is liberated both with silver and with copper anodes at the current densities employed.

Experiments with Anode of other Metal.

With a Zinc Anode.—No iodine is liberated except when a high current density is used ; with moderate current densities zinc is dissolved and is found afterwards in the solution surrounding the anode.

With an Anode of Iron Wire.—The behaviour of the solution appeared to depend on the previous history of the electrode ; thus in several experiments it was found that it sometimes happened that iodine was liberated from the anode, whilst at other times, with the same electrode, no iodine would be liberated, but a dark greenish-black solution would be formed in the immediate neighbourhood of the anode. This solution could be decolorised by reversing the current, and the presence of iron in the coloured solution was repeatedly demonstrated.

With iron the behaviour is therefore erratic, and suggests the ordinary behaviour of iron in aqueous solutions and the passivity of iron.

It is interesting to note that both zinc and iron iodides are only very slightly soluble in liquefied sulphur dioxide, and their solution in the experiments described must be accompanied by the formation of some soluble complex salt with the potassium iodide already in solution.

In the investigation of the electrolysis of potassium iodide in sulphur dioxide two series of quantitative experiments were carried out.

The first had for its object the examination of the properties of the deposit which is formed on the cathode when the solution is electrolysed, and the second the examination of the permanent gas which is liberated at the cathode when current densities of a sufficient magnitude to boil the solution are employed.

The Nature of the Solid Deposit.

In these experiments the electrolysis was carried out in an apparatus consisting of a pair of glass tubes of about 2 cm. internal diameter, connected by a narrower tube of about 8 mm. internal diameter. The wider tubes were closed at the top by means of carefully ground glass joints, through which the wires carrying the electrodes were sealed. To one of these ground glass attachments a side tube was sealed containing phosphoric anhydride. Before carrying out an experiment the potassium iodide which was to be dissolved was strongly heated and then placed at the bottom of one of the tubes of the apparatus, the phosphoric anhydride attachment inserted, and the apparatus exhausted. The exhausted apparatus was then heated to 95° C. for about twelve hours. It was then cooled and immersed in a bath of liquefied ammonia and the sulphur dioxide distilled in through a long column of phosphoric anhydride. This general method of procedure was adopted in all the experiments that were carried out, and the effect of dissolved water vapour was in this way eliminated.

The cathode consisted of a piece of platinum foil which could be suspended from the wire which passed through the ground-glass stopper, and could be removed and weighed before and after each experiment.

An examination of the cathode after the first experiment showed that the deposit was partially soluble in water, that the solution smelt strongly of sulphur dioxide, and that it contained suspended solid matter which proved to be sulphur, and a series of experiments was therefore carried out in which current was passed through the solution and through a silver voltameter in

series, the object being to determine the relation between the amount of silver deposited in an aqueous solution and the amount of sulphur deposited by the same current in the sulphur dioxide solution.

The results of the experiments are contained in the following table :—

TABLE I.

No. of Experiment.	No. of Milligram Equivalents deposited.			Ratios.	
	Of Ag in H_2O Solution.	Of K in SO_2.	Of S in SO_2.	K in SO_2. Ag in H_2O.	S in SO_2. Ag in H_2O.
1	0·58	—	0·33	—	0·57
2	1·06	—	0·70	—	0·65
3	1·15	—	0·64	—	0·56
4	Experiment lost.				
5	0·513	0·483	0·25	0·94	0·49
6	0·527	0·495	0·25	0·94	0·475

These experiments show conclusively that sulphur is always deposited on the cathode when a solution of potassium iodide is electrolysed, but that it is not possible to obtain quantities corresponding with those indicated by Faraday's law. This is sufficiently accounted for by the known solubility of sulphur in sulphur dioxide.

Qualitative experiments showed that the crystalline deposit on the cathode when dissolved in water and filtered from the separated sulphur, and treated with dilute acids, yielded sulphur dioxide and a very small quantity of sulphur, and that the solution contained potassium. This indicated that in addition to the sulphur the deposit contained some potassium sulphite and a small quantity of the potassium salt of an acid richer in sulphur, probably potassium thiosulphate. Experiments 5 and 6 of Table I. were therefore carried out to determine the ratio of the equivalent of potassium and silver.

Considering the difficulty of obtaining an adherent deposit on the cathode, these experiments may be taken as indicating the equivalence of the deposit value in the two solutions.

In several of the experiments that have been described a pair of platinum electrodes was placed in the neighbourhood of the cathode during the experiment, and the conductivity of the solution was measured from time to time during electrolysis. The conductivity fell in every case.

We may summarise the result of this series of experiments as follows :—

1. Sulphur is always deposited at the cathode, but the quantity cannot be accurately determined owing to its solubility in the solvent.

2. A salt deposit consisting largely of potassium sulphite is formed on the cathode in quantities which are equivalent in potassium content to the quantity of silver deposited from an aqueous solution of silver nitrate by the same current.

3. The conductivity of the solution in the immediate neighbourhood of the cathode is lowered during the changes which occur.

The explanation of these facts is immediately forthcoming if we consider them side by side with those which occur at the cathode during the electrolysis of the same salt (potassium iodide) in aqueous solution. This has been done in the following table :—

Changes at Cathode during Electrolysis of Potassium Iodide dissolved in—

(*a*) *Water.*	(*b*) SO_2.
1. Hydrogen liberated equivalent to Ag in voltameter.	Sulphur liberated.
2. Potassium hydroxide formed equivalent to Ag in voltameter.	Potassium sulphite (or thiosulphate) formed equivalent to Ag in voltameter.
3. Conductivity increased due to *increase* in salt concentration at cathode from formation of soluble potassium hydroxide.	Conductivity diminished due to *decrease* in salt concentration at cathode from formation of insoluble potassium sulphite (or thiosulphate).

From this it will be seen that if the liberation of gaseous hydrogen during the electrolysis of aqueous solutions furnishes any evidence for the existence of hydrogen ions in water, the corresponding evidence for the existence of sulphur cations in a solution in liquefied sulphur dioxide is furnished by the liberation of sulphur. Just as in aqueous solution we represent the formation of potassium hydroxide as a combination of the potassium ions which reach the cathode with the hydroxyl ions which have been formed from the water by the discharge of hydrogen ions, so also must we picture the formation of potassium sulphite in sulphur dioxide solutions as a combination of the potassium ions with the minute number of sulphite ions which are formed by the discharge of the sulphur ions.

From these considerations we see that potassium sulphite bears the same formal relation to the solvent sulphur dioxide as potassium hydroxide does to water, but that it is rather to be compared with the insoluble than with the soluble hydroxides, and a closer analogy would be obtained by comparing its formation with that of magnesium hydroxide when a magnesium salt is electrolysed.

The Nature of the Gas.

The gas that is evolved in small quantity at the cathode when moist solutions in sulphur dioxide are electrolysed was found to consist of an explosive mixture of hydrogen, oxygen, and nitrogen. When carefully dried materials are used no gas is evolved unless the current density at the cathode is so great that the liquid boils at this point. When this happens a small quantity of gas is evolved, which, after an examination which was prolonged by reason of the difficulty of obtaining and of analysing the small quantities obtained, was proved to consist of a mixture of nitrogen and oxygen considerably richer in nitrogen than ordinary air. It obviously consisted of dissolved air which was boiled out from the solution surrounding the cathode. The hydrogen of the earlier experiments was traced to the presence of traces of water.

Electrolysis of Tetramethylammonium Iodide and Trimethylsulphonium Iodide.

The experiments with these two substances were approached with considerable interest, as it was thought possible that their electrolysis might result in the formation at the cathode of compounds such as ditetramethylammonium and ditrimethylsulphonium. As it was thought that these compounds, even if formed, would probably be unstable at high temperatures, easily decomposed by water, and readily oxidised by atmospheric air, experi-

ments were planned whereby all operations could be carried out at —35° and in a vacuum. As this latter condition involved the continuous pumping away of considerable quantities of SO_2 a special automatic mercury pump was designed and constructed.*

Preliminary experiments showed that in the case of each of these substances there is formed at the cathode a dark blood-red solution, the colour of which is very readily discharged. The conditions necessary for its discharge were first investigated, and it was found that—

(*a*) The colour is not discharged by dilution with sulphur dioxide.

(*b*) The colour is not discharged by prolonged standing.

(*c*) The colour is discharged immediately by the addition of moist liquid sulphur dioxide, and

(*d*) Slowly by contact with dry air.

(*e*) The colour is discharged and a yellow precipitate formed by mixing together the cathode and anode solutions.

Experiments were therefore planned and the necessary apparatus was designed and constructed to find out, if possible—

(*a*) What is the nature of the compound contained in the red solution.

(*b*) What is the nature of the yellow precipitate formed on mixing the cathode and anode solutions.

Investigation of the Nature of the Compound or Compounds contained in the Red Solution.

Several experiments were carried out, in all of which an apparatus was used which had been specially designed and constructed to admit of the following operations being carried out :—

1. The apparatus and previously heated tetramethylammonium iodide could be exhausted with a phosphorus pentoxide tube attached and left in this condition at 95° C. for twenty-four hours to ensure thorough drying of the materials.

2. The solution for electrolysis could be made in the dried apparatus by admitting sulphur dioxide gas through a stopcock and condensing it in the apparatus on to the dried tetramethylammonium iodide. In some of the experiments the sulphur dioxide was previously purified and dried by distilling it from the metal cylinder into a receiver containing phosphorus pentoxide, leaving it in contact with the latter overnight, and finally distilling it from this receiver through a long column of phosphorus pentoxide into the electrolysing apparatus.

3. The solution made as described, with complete exclusion of air and moisture, could be electrolysed in an atmosphere of sulphur dioxide at the vapour pressure of the solution, no air being admitted.

4. The red cathode solution, after electrolysis had been carried on for the desired time, could be transferred, without opening the apparatus, into a special receptacle, which could then be sealed off from the main apparatus. The solution in this receptacle then contained the compound or compounds which were to be investigated and the solution had at no time been subjected to a temperature higher than —33° C. (boiling-point of liquefied ammonia), nor had it been exposed to contact with any substance other than the glass of the containing vessel. It had not passed through any stopcocks and therefore could not contain anything but the original salt and the products of its electrolysis.

5. The next stage in the operation was the evaporation of the solution and

* Steele, *Phil. Mag.*, June, 1910.

the examination of the residue. In order to effect the former, the receptacle had been provided with a tube and stopcock. This tube was now attached to the automatic pump, and after the bulb and attachments of the latter had been thoroughly exhausted, the stopcock was opened and the sulphur dioxide removed through the pump, the receiver being kept immersed in a bath of liquefied ammonia.

Fig. 1 represents the type of apparatus used for the electrolysis experiments. The portion *B* was added when it was desired to separate either

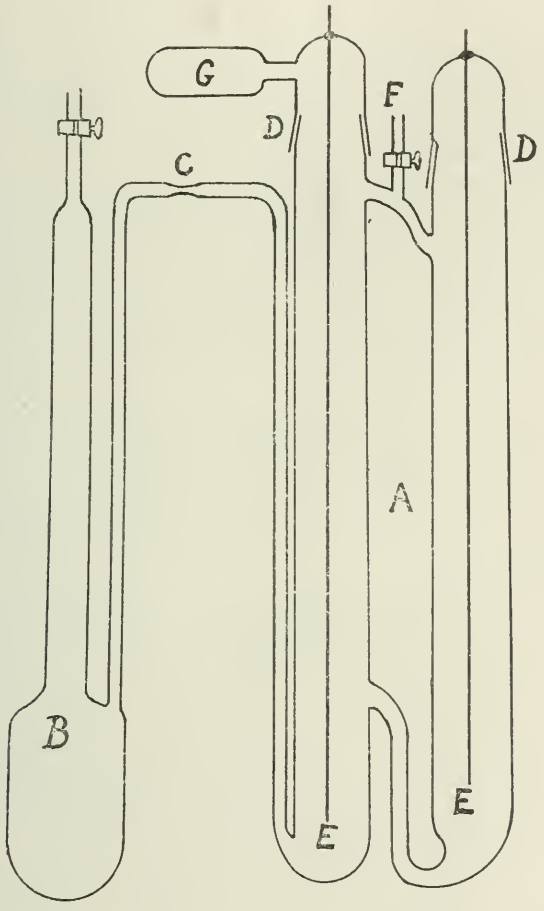

Fig. 1.

anode or cathode solution for examination. The solution could be drawn over from *A*, which is the actual electrolysis vessel, into *B*, by slight variation of the temperature of the two vessels with consequent variation of vapour pressure. *B* could be sealed off at *C* by a small blow-pipe flame. *EE* represent the electrodes. *DD* are ground caps to allow of the insertion of solids and the removal of the electrodes. Sulphur dioxide was distilled in through a tube containing phosphorus pentoxide, sealed to the tap *F*. *G* is a phosphoric oxide tube for drying the apparatus.

The possibility that a compound such as $(N(Me)_4)_2$, even if formed during electrolysis, might be decomposed during the subsequent evaporation was investigated. Should such a decomposition occur, it is almost certain that the products would include ethane, and accordingly the sulphur dioxide as it was pumped away was tested occasionally to see if any permanent gas could be detected, and in no case was even the smallest trace of such found. It is therefore concluded that no such decomposition occurs.

During the evaporation of the solution the dark red colour is retained until no liquid is left. If the exhaustion is stopped at this stage there remains a solid residue of a very dark brown, almost black substance. At the temperature of the bath the vapour pressure of this substance is about 3·5 mm. of mercury, and on continuing the exhaustion the pressure remains nearly constant at this value, but as the gas is removed from the vessel the colour of the solid substance gradually changes from dark brown to pale yellow. At this stage the gas that was removed was very carefully examined for permanent gases, but none were ever found.

The practical constancy of the sulphur dioxide vapour pressure during exhaustion pointed to the dark brown solid as being simply a compound of the yellow one with sulphur dioxide, and to test this assumption dry sulphur dioxide was admitted to the vessel containing the yellow solid to see if the dark brown substance could be reproduced. It was found that sulphur dioxide was absorbed, but the colour of the compound formed was a pale red. Whether another modification of the original compound or a fresh compound was formed was not determined.

This yellow residue was obtained in about eight experiments, and its properties were examined in various ways. It was found that it never contained more than a trace of iodide, thus showing that separation of the cathode solution had been efficiently carried out. The substance always smelt strongly of sulphur dioxide, was not hygroscopic, and in the case of samples from which the gas had not been continuously pumped away for a prolonged period, it evolved sulphur dioxide on adding to water.

All solutions of the substance were found to leave a residue of sulphur on standing and some samples rapidly deposited sulphur shortly after solution. The samples which behaved in this manner were found to be very strongly reducing and gave reactions very similar to those of thiosulphate. The reducing value of the substance was determined by titration with $\frac{N}{20}$ iodine solution, and the solution after titration was found to be strongly acid. This is the characteristic behaviour of sulphites when titrated with iodine. The amount of sulphite present was determined by combining the results of the iodine and acidity titrations, and the result of the analyses of the different samples is shown in the following summary :—

Experiment 1.—*Analysis carried out immediately after solution.* Iodine reducing value was due to sulphite 87 per cent. and thiosulphate or other reducing agent 13 per cent.

Experiment 2.—*Analysis made after the solution had stood some time.* Reducing action entirely due to sulphite.

Experiments 3 *and* 4.—*Analysis made before the deposition of sulphur was complete.*

Experiment 3.—Reduction due to sulphite 93 per cent. Other substances 7 per cent.

Experiment 4.—Reduction due to sulphite 94·5 per cent. and other substances 5·5 per cent.

The substance is obviously composed mainly of tetramethylammonium

sulphite, formed at the cathode, together with a small quantity of some extremely easily decomposed and highly reducing substance formed also at the cathode by the interaction of the discharged sulphur. It is probable that the red colour, which is characteristic of this cathode solution and which is so easily destroyed, is a property of this easily decomposed compound.

Similar experiments to those recorded in the foregoing summary were carried out with trimethylsulphonium iodine and the results, both qualitatively and quantitatively, were the same, namely, a blood-red liquid was formed at the cathode. From this a pale yellow solid was obtained by evaporating off the sulphur dioxide, and this solid, when treated with water, left a residue of sulphur, and the aqueous solution was found to contain sulphite and a very small proportion of a very highly reducing substance which rapidly decomposed with deposition of sulphur.

The Yellow Precipitate formed on mixing the Cathode and Anode Solutions.

The anode employed in the foregoing experiments was of zinc, which dissolved during the action, and it was therefore probable that the precipitate was a zinc compound. To test this, a solution of zinc bromide and tetramethylammonium iodide in sulphur dioxide was added to a small quantity of the cathode solution and an immediate yellow precipitation occurred.

The experiment, in which the compound was prepared, was carried out in an apparatus specially designed and constructed for the purpose of making the solutions by electrolysis, subsequently mixing the cathode and anode solutions and transferring the mixture of solution and suspended precipitate to another specially designed and constructed apparatus in which it could be washed repeatedly with fresh quantities of pure sulphur dioxide, all the operations being conducted in a dry exhausted atmosphere. The precipitate thus prepared was washed seven or eight times, or until the filtrate of sulphur dioxide came through colourless, and it was then dried whilst still in the apparatus, and finally removed for analysis.

The results of the analysis are as follows :—

Sulphur estimated as sulphur dioxide, 19·13 per cent.
Sulphur estimated as sulphate, 20·8 per cent.
Zinc estimated as oxide (two samples), 28·6 and 29·6 per cent.
Theory requires for $Zn_3(NMe_4)_2(So_3)_4$ S = 19·3 per cent.
Zn = 29·5 per cent.

The high result of the sulphur estimation as sulphate might be due to the presence of a small amount of free sulphur in the precipitate, and is in accord with the general experience of the foregoing analyses.

It is interesting to observe the formation of this particular double salt as an insoluble precipitate in liquefied sulphur dioxide, corresponding potassium and ammonium salts having been prepared in aqueous solution and examined by Berglund.*

Electrolysis of Tetramethylammonium Sulphite.

For these experiments a sample of tetramethylammonium sulphite was prepared from the iodide by first precipitating the latter with moist silver hydroxide, filtering off the silver iodide, and evaporating the bulk of the water from the filtrate.

The very concentrated solution of tetramethylammonium hydroxide was then placed in the apparatus in which the electrolysis was to be carried out and sulphur dioxide passed in in sufficient quantities to combine with all the

* Ber., 1874, 7, 469.

tetramethylammonium hydroxide and to displace all the air. The apparatus was then exhausted, after being connected to a tube charged with phosphoric anhydride. When all the water had been removed sulphur dioxide was distilled into the apparatus so as to make with the dry sulphite a water-free solution for electrolysis.

The sulphite is freely soluble in sulphur dioxide, forming a deep yellowish red solution. On electrolysis, the characteristic blood-red solution containing sulphur is formed at the cathode.

Tetramethylammonium sulphate is also soluble in sulphur dioxide, forming a good conducting solution, which on electrolysis yields the same characteristic red cathode solution as is produced by the iodide and sulphite.

Electrolysis of Hydrogen Bromide.

Hydrogen bromide appears to be freely soluble in sulphur dioxide, but if quite dry the solution is almost non-conducting, in this respect presenting a great contrast to the corresponding solutions in water.

If the solution contains as an impurity either water or certain organic compounds, the current flows freely with any metal as electrode, the products of electrolysis being hydrogen at the cathode and bromine at the anode. This behaviour is probably to be attributed to interaction between the hydrogen bromide and the second solute resulting in the formation of an oxonium compound, which acts as a good electrolyte.

Oxonium compounds have been investigated by a number of investigators, and especially by Collie and Tickle, Baeyer and Williger, and Archibald and McIntosh.

The last-named workers, for example, have isolated and examined a number of compounds of hydrogen bromide or iodide with compounds such as ether, acetone, and generally with the alcohols, ethers, and ketones.

It has been already noted that hydrogen bromide when dissolved in liquefied sulphur dioxide does not form a highly conducting solution, and experiments have shown that the same may be said of the sulphur dioxide solutions of the following substances :—

Dimethylpyrone,	Acetone,	Benzophenone,
Benzaldehyde,	Ether,	Water,

and M. dinitrobenzene, but when small quantities of hydrogen bromide are added to solutions of either of the first six compounds enumerated above, good conducting solutions result; with M. dinitrobenzene there is no appreciable change in conductivity.

The compound of dimethylpyrone and hydrogen bromide was isolated and examined by Collie and Tickle; those of acetone and ether with hydrogen bromide were isolated and examined by Archibald and McIntosh, and there can be no doubt that the increase of conductivity in the case of these compounds and in the case of benzaphenone and benzaldehyde is due to the formation of these oxonium compounds. If this is granted, we must accept the same explanation for the case of water.

The view that combination of water and hydrogen bromide is an antecedent to conduction is strongly confirmed by the behaviour of mixed solutions of these substances when electrolysed. When water is added to a solution of hydrogen bromide in sulphur dioxide, a small quantity dissolves in the solution, the remainder dissolving some hydrogen bromide and sinking to the bottom as a heavy liquid, which may sometimes crystallise as a white solid which melts below the boiling-point of the sulphur dioxide. This solid is probably one of the hydrates of hydrogen bromide which are known to exist at low temperatures.

When a current is passed through such a saturated solution, small droplets appear on the cathode, increase in size, and fall to the bottom, producing a liquid similar in properties to the solution of hydrogen bromide in water previously mentioned.

If the scheme suggested below, in which water takes part in the conduction, be correct, water should be carried to the cathode, and in a saturated solution be precipitated there. At the same time the anode solution should lose water and become unsaturated. To test this an H-shaped electrolysis vessel was constructed, filled with solution, and an excess of water placed in the anode limb. A stopper was fitted in the tube connecting the two limbs. After passing the current for some time the anode and cathode solutions were separated by means of this stopper and the solutions stirred. The quantity of undissolved water in the anode limb was found to have decreased, that in the cathode limb to have increased.

On account of the many similarities between hydrogen sulphide and water it was considered possible that a solution of hydrogen sulphide in a mixture of sulphur dioxide and hydrogen sulphide might be conducting.

It was found that sulphur dioxide and hydrogen sulphide did not react in the gaseous state if even moderately dry. Passage rapidly through five or six cm. of phosphoric oxide dried the gases sufficiently. It was found possible to condense the liquids together at — 80° and to prepare solutions of hydrogen sulphide in sulphur dioxide at temperatures up to the boiling-point of that liquid without reaction taking place, in an apparatus dried in a water oven and cooled in air.

A solution so prepared was almost non-conducting, and the addition of hydrogen bromide caused practically no increase in the current.

These results are entirely consistent with the following representation of the reactions that take place :—

1. $H_2O + HBr \rightleftarrows H_3OBr$, oxonium bromide.
2. $H_3OBr \rightleftarrows H_3O^{\cdot} + Br'$, and during electrolysis.
3. $2H_3O^{\cdot} + 2\theta \longrightarrow H_2 + 2H_2O$ (at cathode).
4. $2Br' - 2\theta \longrightarrow Br_2$ (at anode).

This series of reactions is extremely interesting as indicating the probability that hydrogen bromide (and inferentially the other halogen hydrides) does not in itself act as an electrolyte, but must first enter into combination with water, or ammonia, or with some compound with which it can form oxonium or ammonium compounds.

Thus when hydrogen bromide dissolves in liquefied ammonia it would be readily conceded that the resulting solution contains ammonium bromide, and when it dissolves in water we must be prepared to recognise the similar formation of oxonium bromide, probably very much dissociated, at the ordinary temperature. The non-formation of a conducting solution when hydrogen bromide is dissolved in the other halogen hydrides or in liquefied sulphur dioxide is probably due, at least in part, to the non-formation of such compounds.

Measurements have been made of the conductivities of sulphur dioxide containing in solution various mixtures of hydrogen bromide and the substances enumerated above, a special apparatus having been made to permit of the preparation of solutions of known strength with carefully dried materials. All the sulphur dioxide used was distilled into the apparatus through a long column of phosphorus pentoxide. The conductivities were determined at a temperature of — 35° C.

The cell constant = 0·059.

The specific conductivity, K, of pure sulphur dioxide = $1{\cdot}5 \times 10$ mhos.

As stated previously, water is not very soluble in a mixture of hydrogen bromide and sulphur dioxide. As time did not permit of determinations of the solubility of the water, the value for the molecular conductivity only represents the minimum possible and is really too low, excess of water having been added.

TABLE II.

Molecular Conductivities.

Gram. Mols. HBr.	Of	Dissolved in v Gram. of SO_2.	Dilution.	Specific Conductivity.	Molecular Conductivity.
	Ether.				
0·0	0·0051	9·72	$1{\cdot}25 \times 10^{+3}$	$1{\cdot}18 \times 10^{-4}$	$1{\cdot}47 \times 10^{-1}$
0·049	0·0051	19·5	$2{\cdot}5 \times 10^{3}$	$1{\cdot}4 \times 10^{-3}$	3·50
0·049	0·0051	9·72	$1{\cdot}25 \times 10^{3}$	$2{\cdot}95 \times 10^{-3}$	3·69
	Dimethylpyrone.				
0·0	0·0011	10·17	$6{\cdot}1 \times 10^{+3}$	$1{\cdot}5 \times 10^{-4}$	$9{\cdot}15 \times 10^{-1}$
0·011	0·0011	10·17	$6{\cdot}1 \times 10^{3}$	$2{\cdot}8 \times 10^{-3}$	$1{\cdot}74 \times 10$
0·011	0·0011	19·00	$1{\cdot}14 \times 10^{4}$	$1{\cdot}47 \times 10^{-3}$	$1{\cdot}67 \times 10$
0·011	0·0011	33·8	$2{\cdot}02 \times 10^{4}$	$0{\cdot}908 \times 10^{-3}$	$1{\cdot}83 \times 10$
	M. dinitrobenzene				
0·0	0·00595	10·00	$1{\cdot}100 \times 10^{3}$	$1{\cdot}48 \times 10^{-4}$	$1{\cdot}63 \times 10^{-1}$
0·025	0·00595	10·00	$1{\cdot}100 \times 10^{3}$	$1{\cdot}50 \times 10^{-4}$	$1{\cdot}65 \times 10$
	Acetone.				
0·0	0·007	9·5	$9{\cdot}0 \times 10^{2}$	$5{\cdot}9 \times 10^{-5}$	$5{\cdot}3 \times 10^{-3}$
0·016	0·007	9·5	$9{\cdot}0 \times 10^{2}$	$1{\cdot}85 \times 10^{-2}$	$1{\cdot}67 \times 10$
0·016	0·007	20·34	$1{\cdot}9 \times 10^{3}$	$7{\cdot}46 \times 10^{-3}$	$1{\cdot}43 \times 10$
	Benzophenone.				
0·00	0·00055	10·37	$1{\cdot}24 \times 10^{4}$	$2{\cdot}0 \times 10^{-6}$	$3{\cdot}72 \times 10^{-2}$
0·02	0·00055	10·37	$1{\cdot}24 \times 10^{4}$	$3{\cdot}75 \times 10^{-4}$	$1{\cdot}08 \times 10$
0·02	0·0033	24·67	$4{\cdot}92 \times 10^{3}$	$2{\cdot}04 \times 10^{-3}$	$0{\cdot}98 \times 10$
0·02	0·0033	10·37	$2{\cdot}06 \times 10^{3}$	$4{\cdot}62 \times 10^{-3}$	$0{\cdot}952 \times 10$
	Benzaldehyde.				
0·00	0·005	10·0	$1{\cdot}31 \times 10^{3}$	$1{\cdot}95 \times 10^{-3}$	$2{\cdot}54 \times 10^{-2}$
0·025	0·005	10·0	$1{\cdot}31 \times 10^{3}$	$4{\cdot}72 \times 10^{-3}$	6·17
0·025	0·005	21·9	$2{\cdot}88 \times 10^{3}$	$2{\cdot}42 \times 10^{-3}$	6·95
0·025	0·0283	21·9	$(5{\cdot}75 \times 10^{3})$	$1{\cdot}25 \times 10^{-2}$	(7·15)
	Water.				
·035	0	9·8	$1{\cdot}86 \times 10^{2}$	$1{\cdot}5 \times 10^{-4}$	$2{\cdot}8 \times 10^{-2}$
0	·0083	9·8	$7{\cdot}83 \times 10^{2}$	$1{\cdot}5 \times 10^{-5}$	—
·035	·0083	9·8	$7{\cdot}83 \times 10^{2}$	$4{\cdot}2 \times 10^{-3}$	> 3·3

The results of the measurements are collected in Table II., which shows the number of gram molecules of hydrogen bromide, of water, or other solute, or of both, which are dissolved in the stated weight of sulphur dioxide.

The fourth column contains the dilution of the solution expressed as the number of c.c.'s of solution containing one gram molecule of dissolved substance.

The fifth column contains the values of the specific conductivities of the various solutions, and the molecular conductivities are given in the last column.

The molecular conductivities which are given in the case of the mixed solutions are those of the water or other organic solvent, with the exception of the most concentrated solution of benzaldehyde, the concentration of which is greater than that of the hydrogen bromide. In this case the figures in brackets refer to the volume containing one gram mol of hydrogen bromide and the corresponding molecular conductivity.

TABLE III.

Some Molecular Conductivities Compared.

1. KCl in H_2O, 125.
2. HBr in SO_2, ·0405.
3. Acetone in SO_2, ·0053.
4. HBr Acetone in SO_2, 16·7.
5. HBr Ether in SO_2, 3·7.
6. HBr Dimethylpyrone in SO_2, 17·4.
7. HBr Benzaldehyde, 6·95.
8. HBr Benzophenone, 10·8.
9. $HBrH_2O$ in SO_2, > 3·3.

In order to convey a clear idea of the actual magnitude of the conductivities of these solutions a few molecular conductivities have been collected in Table III. It will be seen that the molecular conductivity of a mixture of water and hydrogen bromide in sulphur dioxide is of the same order of magnitude as that of a 1 per cent. solution of acetic acid in water (3·5), while the specific conductivity (4×10^{-3}) is several times greater than that of the acetic acid solution at 18° ($5{\cdot}8 \times 10^{-4}$).

In all cases but one the quantity of hydrogen bromide is considerably in

TABLE IV.

Variation of Molecular Conductivity with Time.

Solution containing		Time in Minutes after Mixing.	Mol. Conductivity.
H_2O ·0083 gr. mols	... } 780	0	3·31
HBr ·035 gr. mols in 6·5 c.c. of SO_2...	... }	30	2·72
Ether ·0051 gr. mols	... } 1,250	0	3·68
HBr ·049 gr. mols in 6·4 c.c. of SO_2	... }	90	4·56
Acetone ·007 gr. mols...	... } 900	0	14·8
HBr ·010 gr. mols in 6·23 c.c. of SO_2	... }	25	16·5
Acetone ·007 gr. mols	... } 1,900	0	14·2
HBr ·016 gr. mols in 13·4 c.c. of SO_2	... }	40	17·3

excess of that required for combination with the other solute, and the dilution has been calculated on the assumption that practically all of the water or organic solute has combined with the hydrogen bromide.

The figures for meta dinitrobenzene indicate that no combination of the two compounds is brought about. It has been found that the conductivity of certain solutions varies with time, and this variation is well shown by the following figures, Table IV., which refer to experiments with water, with ether, and with acetone.

When a water mixture was allowed to stand for several hours a heavy oily liquid appeared at the bottom. The fall in conductivity might be attributed to the slow formation of this substance, which in general properties corresponded with sulphur bromide. It is hoped to investigate the nature of the substance more fully at a later date.

The rise in molecular conductivity which occurs with the other substances is consistent with the supposition that the velocity of the formation of the oxonium compound is not instantaneous, the conductivity rising with the increase in concentration of the compound.

Electrolysis of Solutions of Ether and HBr in SO_2.

With ether solutions current flowed freely, but at the start of the experiment very little hydrogen was evolved. After the current had passed for some time (an hour or two) much more gas could be collected. Quantities up to about two-thirds of the theoretical amount were collected from solutions which had previously been electrolysed for some time.

With water solutions more gas was evolved at the commencement of the electrolysis, approximately half the theoretical volume, but this quantity did not increase with continual passage of the current.

The fact that hydrogen is not evolved in theoretical volume may be explained by the suggestion that some is used up in the formation of reduction products.

In view of its possible bearing on the nature of the hydrogen ion and on the general theory of electrolysis, it is hoped to extend that portion of the work dealing with the conductivity and electrolysis of hydrogen bromide solutions at a later date.

Electrolysis of Potassium Mercury Iodide.

Qualitative attempts were made to electrolyse solutions of certain double salts, as, for example, the double compound of potassium and mercury iodides. It was found that this compound behaved very similarly to potassium iodide : a deposit containing sulphur being formed on the cathode, and the current falling very rapidly to the usual small value. In one experiment, in which the materials had not been carefully dried, it was found that mercury was deposited as a film on a strip of copper immersed in the solution, but when the experiment was repeated with carefully dried materials no such effect could be produced.

Electrode Potentials of the Metals.

The programme mapped out for the determination of the electrode potentials was as follows :—

1. To determine the electrode potentials of metals when immersed in saturated solutions of their salts.

2. To determine the solubility of these various salts, using for the purpose the microbalance recently described by Steele and Grant.*

3. To determine the conductivities of extremely dilute solutions of these salts, and so to ascertain the ionic concentrations of the various metallic ions.

From the data thus obtained it should be possible to calculate the normal electrode potentials of the metals when dissolved in a solvent such as sulphur dioxide, which contains no hydrogen, and to compare the values thus determined with those obtained in aqueous solutions.

Owing to the removal of one of us from Melbourne to Brisbane, and the

* *Proceedings of the Royal Society*, 1909, A 82, p. 580.

consequent temporary loss of facilities for experimental work, this programme has been interrupted, and the only part actually carried out is the measurement of the electrode potential of metals immersed in saturated solutions of their salts.

The choice of metals and salts was limited in the first place by the fact that the only freely soluble metallic salts are the bromides and iodides of the alkali metals, and that these are not capable of being used for electrodes on account of their rapid tarnishing in an atmosphere of dry sulphur dioxide.

On the other hand, the salts of other metals being extremely insoluble, cells prepared with saturated solutions of these salts have an extraordinarily small capacity. As a consequence of this, it was found to be impossible to determine the e.m.f. of these combinations by the usual potentiometer method, since the minute amount of current taken out of the cells during the measurement immediately lowered the e.m.f. to zero.

The measurements were therefore carried out with a quadrant electrometer, one pair of quadrants being earthed and the other connected with one electrode of the cell, the other electrode being earthed. The electrometer was one of very small capacity, and it was found that no polarisation was produced in the cell when its e.m.f. was measured by this method. It was not found possible to use the ordinary dipping electrode vessels, and therefore an apparatus was designed for the measurements. This apparatus consisted of two electrode vessels immersed in a wide test-tube. One of these vessels is shown in Fig. 2. It consists of an H-shaped tube, one limb of which, *A*, is closed at the bottom, the other, *B*, being open. The open limb is provided with a ground-in hollow glass stopper, *C*, with a hole drilled in it opposite the connecting tube, *D*, and by rotating this stopper the solution contained in the closed limb could be brought into communication with the liquid in the wide test-tube *E*.

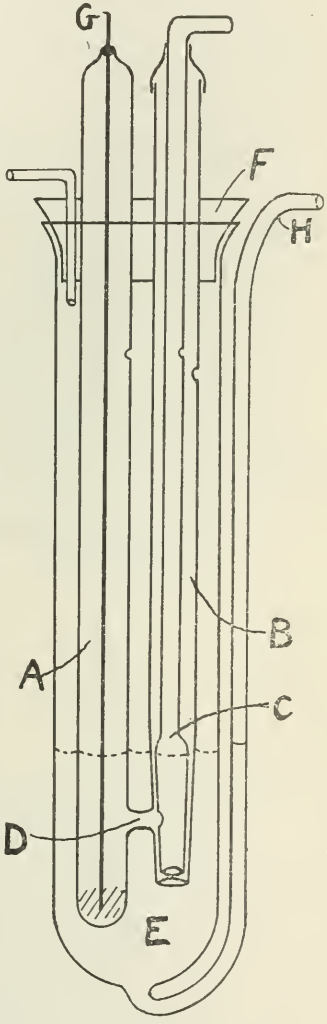

Fig. 2.

The two electrode vessels were fitted in a rubber cork, *F*, which in its turn fitted the test-tube, and the whole could be immersed in a Dewar flask containing liquefied ammonia.

In carrying out an experiment, the electrodes, *G*, which were composed of a wire of the metal under investigation, were placed in the closed limb of the H tube, a small portion of the selected salt of the metal having been first placed in the same limb. The upper end of the tube containing the wire was then sealed with sealing-wax and the apparatus exhausted and dried. When

it was judged that the whole apparatus was thoroughly dry, it was immersed in a bath of liquefied ammonia, the electrode vessels placed in communication with the test-tube by turning the stopper, and sulphur dioxide distilled into the apparatus through *H*. The sulphur dioxide filled the test-tube to the required level and overflowed into the electrode vessels, forming there after the lapse of a few hours a saturated solution of the salt in question. It was usually found that the film of sulphur dioxide surrounding the stopper was sufficiently conducting to allow of readings being taken without polarisation effect being observed.

The materials employed were from various sources, and were subjected to various methods of purification, with the object of testing whether the effects measured were due to the presence of minute quantities of impurities.

A sufficient number of measurements have been made to indicate that each metal has a definite electrode potential when immersed in liquefied sulphur dioxide, and that the magnitude of the potential is affected by the concentration of the metallic ion in solution in the same manner and in the same direction as it is in aqueous solution.

The measurements that are described were made at a temperature of $-35°$ C. The deflections of the electrometer were standardised by means of a standard Clark cell. The standard electrode employed was one of mercury, covered with a layer of purified mercurous chloride, made into a paste with liquefied sulphur dioxide.

The following measurements of the e.m.f. of a typical cell are given as an example of the degree of constancy of e.m.f. which can be obtained with the extremely dilute solution which it was necessary to employ.

Cell Constancy of Hg/HgCl *in* $SO_2/SO_2/PbCl_2$ *in* SO_2/Pb.

Time Measurement. H.	M.	E.M.F.
0	0	0·40
1	45	0·427
3	15	0·430
5	0	0·437
7	30	0·430
8	45	0·433

A. Pb/$PbCl_2$/HgCl/Hg. Mercury electrode negative.
   1. E.m.f. = 0·435 volt.
   2. Same cell, but freshly prepared and purified materials.
      E.m.f. = 0·435 volts.

B. Zn/$ZnBr_2$/HgCl/Hg. Mercury electrode negative.
   1. Pure zinc cast into rod.
      Zinc bromide distilled.
      E.m.f. 0·38 to 0·40 volt.
   2. Zinc bromide redistilled.
      E.m.f. 0·37 to 0·40 volt.

C. Cd/CdI_2/HgCl/Hg.
   1. Cd metal electrolytic, Schuchardt, cadmium iodide recrystallised.
      E.m.f. 0·42 to 0·445 volt.
   2. Freshly prepared and treated material from the same stock.
      E.m.f. 0·42 to 0·43 volt.

Addition of potassium iodide and of tetramethylammonium iodide to the solution surrounding the cadmium iodide instantly altered the e.m.f., and in all

cases tested the e.m.f. was sensitive to the addition of any salt having an anion common to the added and dissolved salt.

Summary.

In the foregoing pages experiments are described which were designed to ascertain the mechanism of electrolysis in liquefied sulphur dioxide.

1. It has been shown that during the electrolysis of solutions of potassium or sodium iodides, tetramethylammonium iodide, trimethylsulphonium iodide, sulphur is deposited on the cathode, and that a sulphite is simultaneously formed.

2. That, at the anode, changes occur which are analogous to those occurring in aqueous solution. For instance, bromine and iodine are liberated from solutions of bromides and iodides.

3. That anodes of zinc and iron are attacked and pass into solution as complex iodides when iodides are electrolysed.

4. Evidence has been adduced to show that water and hydrogen bromide unite to form an oxonium compound which is electrolytic in character, and this evidence has been strengthened by comparison with the behaviour of several well-known oxonium compounds.

5. A few electrode potentials of metals immersed in saturated solution of their salts have been measured.

In conclusion, the authors wish to express their thanks to the Government Grant Committee of the Royal Society for a grant made to one of us by means of which a large portion of the expense of the work has been met. We also wish to express our thanks to Messrs. Felton, Grimwade & Co. for their kindness in presenting us with large quantities of liquefied ammonia.

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VAPOUR-PRESSURE OF CONCENTRATED AQUEOUS SOLUTIONS.

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AND

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(*A Paper read before the Faraday Society, Tuesday, March 26, 1912, Mr. Alexander Siemens, Vice-President, in the Chair.*)

Much work has been done on the vapour-pressure of dilute solutions, but to concentrated solutions little attention has been paid. The Earl of Berkeley and E. G. J. Hartley* made experiments with cane-sugar and with calcium ferrocyanide†; the highest concentrations used were respectively 66 grams in 100 grams water, and 50 grams in 100 grams water. Krauskopf‡ worked with sodium chloride, potassium chloride, and cane-sugar, but the concentration, in the case of the two chlorides, did not exceed 30 grams per 100 grams of water, and in the case of sugar, 60 grams per 100 grams of water.

We have now measured the vapour-pressures of solutions of various concentrations, and the highest concentration has been far higher than that used by other experimenters.

The solutes were electrolytes and non-electrolytes, with and without water of crystallisation, viz.: Urea, cane-sugar, glycerol, raffinose (5 mols H_2O) potassium chloride, and calcium chloride (6 mols H_2O).

The large range of the concentration may be gauged from the fact that the most dilute solution of calcium chloride used contained 5·15 grams of the hexahydrate to 100 grams of water, while the most concentrated solution consisted of the fused hexahydrate. In the case of raffinose the concentration varied from 16 grams to 1,030 grams raffinose to 100 grams of water.

In each case the concentration of the solution was increased until it was the highest possible at the temperature employed, the object being to trace the connection between concentration and vapour-pressure, and, if possible, to throw light on the constitution of solutions.

Callendar§ develops a hydrate theory of solution, the essential point of which is the formation of definite hydrates, according to the fundamental law of chemical combination. He states that if each molecule of the solute appropriates a molecules of solvent, and if n, N denote the whole number of molecules of solute and solvent respectively in the solution, the number of free molecules of solvent is $N - an$, and the whole number of molecules in the solution is $N - an + n$.

Then, if p is the vapour-pressure of the pure solvent, and p^1 that of the solution, $\frac{p^1}{p} = \frac{N - an}{N - an + n}$, from which $a = \frac{N}{n} + \frac{p^1}{p^1 - p}$. This gives a method of determining the hydration factor a. Callendar states that a is a constant within certain limits, and equal to a simple integer. Jones and Bassett‖ state as follows: "According to the older hydrate theory, when a substance like calcium chloride is dissolved in water there are formed certain

* *Proc. Roy. Soc.*, A, vol. 77.
† *Phil. Trans.*, 1909, vol. 209.
‡ *Journ. Phys. Chem.* 1910, **14**, 489.
§ *Proc. Roy. Soc.*, A, **80**, 466.
‖ *Amer. Chem. Journ.*, 1905, **33**.

definite compounds with perfectly definite amounts of water. According to the theory established by this work, the compounds formed are, at best, very unstable, and vary in combination all the way from one molecule of water to a very great number. The composition of the hydrate formed by any given substance is purely a function of the concentration of the solution."

These theories will be presently considered in the light of the results we have now obtained.

Method of Work.—A few determinations were made with urea solutions by the static method, but by far the greater number were made by the air-current

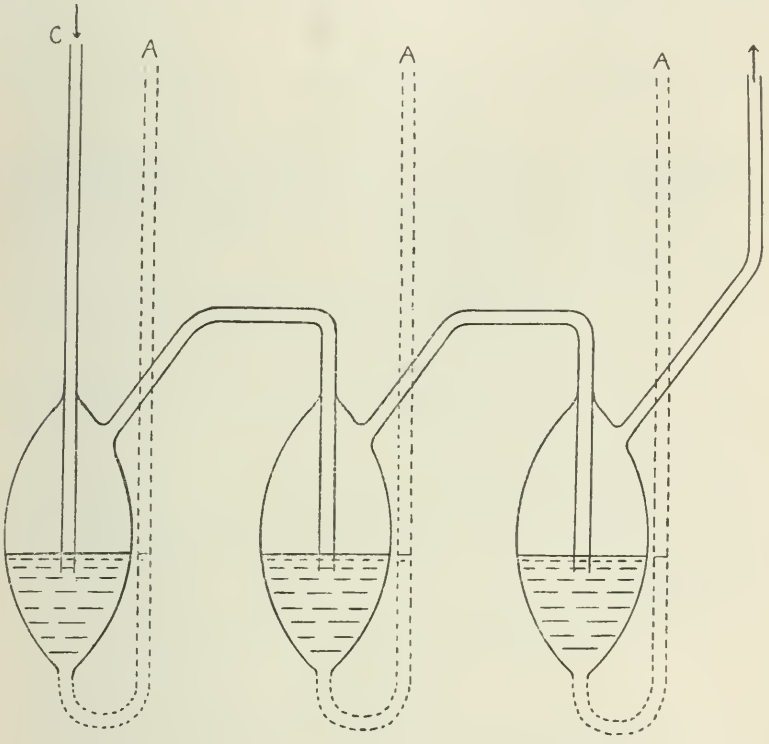


FIG. 1.

method. The apparatus used has been described in a previous paper by one of us,* and details are given there, but the following modifications were introduced.

1. The small wash-bulbs containing water, between the calcium chloride tube and the aspirator, were replaced by a glass tube, 25 cm. in length and 2·5 cm. in diameter, containing small pieces of sponge saturated with water. This was sufficient to saturate with water-vapour the air passing into the aspirator.

2. The solution in the thermostat was contained in three bulbs instead of four, since it was found that complete saturation could be obtained with three bulbs. A new feature was introduced into the bulbs and is shown in the accompanying diagram (Fig. 1). It consists of a glass tube *A* fused to the bottom of each bulb, and then bent so that the top of the tube rose above the level of the liquid in the thermostat. This was found to be a great improvement, since each bulb could now be filled in situ, and independently

* *Proc. Roy. Soc.*, A, vol. 72.

of the other two by means of a funnel attached to A, and emptied by suction. During an experiment the three tubes, A, A, A, were closed by small rubber stoppers, so that all the air which passed through the bulbs came through the proper inlet C.

3. The gauge G_1 was omitted because it was deemed unnecessary, and the gauge G_2 alone was used. The mode of procedure was as follows:—After the bulbs had been filled with the solution the absorption apparatus was placed in position, and the necessary corrections made. A slow stream of air was aspirated through the whole apparatus and the pressure gauge G_2 was read. Then the connection between the absorption apparatus and the bulbs was broken and the gauge read again while the air was being aspirated through the absorption apparatus only. If p_1 and p_2 are the respective pressures recorded by the gauge, P the pressure of the atmosphere, and p the pressure of water vapour at the temperature of the aspirator, the pressure in last bulb $= P - p_1 + p_2$ and pressure of air in aspirator $= P - p_1 - p$.

Measurements were made at 70° C., at 90° C., and in a few cases at 60° C. The weights and thermometers used were those described in the previous paper, and the chemicals, with the exception of raffinose, which was made by Merck, were made by Kahlbaum.

Saturation of the Air by the Vapour.—In addition to those described in the previous paper, the following experiments were made to test whether the air was fully saturated by the vapour when it left the last bulb.

An approximately $\frac{N}{5}$ solution of potassium chloride was placed in the bulbs at 90° C. After the aspiration the solution was drawn off from each bulb separately, and the strength of each estimated by titration with standard silver nitrate solution.

Results.—3·7485 grams potassium chloride were dissolved in water and the solution made up to 250 c.c. Before aspirating, 10 c.c. of this solution required (1) 11·56 c.c., (2) 11·53 c.c., mean = 11·545 c.c., of the silver nitrate solution. Two litres of air were then aspirated through the solution in the bulbs. After aspirating—

10 c.c. from bulb	1	required	12·88	c.c. $AgNO_3$	solution
„	„ 2	„	11·73	„	„
„	„ 3	„	11·55	„	„

After aspirating a further 250 c.c. of air, the figures were:—Bulb 1, 14·12 c.c.; bulb 2, 11·83 c.c.; bulb 3, 11·57 c.c.

It is seen that the strength of the solution in the third bulb did not increase materially after aspirating 2 litres of air through, and hence it is assumed that the air is saturated with water vapour. It should be also noted that the above experiments form an extreme case, since at 90° C. 2 litres of air were drawn through, while in the actual measurement of vapour-pressures only 1 litre was drawn through at that temperature. At the other temperatures (60° C. and 70° C.) 2 litres were drawn through, and in all cases the rate was approximately a litre in half an hour.

The results, with all the data, are given in an appendix.

The values for the vapour-pressure of water which were used for calculating a and M are as follows:—149·32 mm. at 60° C., 233·8 mm. at 70° C., and 525·8 mm. at 90° C. These values were taken from *Physiko-Chemische Messungen*, Ostwald-Luther, Zweite Auflage.

Discussion of Results.—In the accompanying diagram (Fig. 2) the concentrations, expressed as the number of molecules of solute divided by the

number of molecules of solvent, have been plotted against the depressions of vapour-pressure. The curves are numbered as follows :—

Curve.			At °C.
i	is that for	urea	60
ii	„	urea	70
iii	„	glycerol	70
iv	„	cane-sugar	70
v	„	raffinose	70
vi	„	urea	90
vii	„	potassium chloride ...	70
viii	„	cane-sugar	90
ix	„	potassium chloride ...	90
x	„	calcium chloride	70
xi	„	calcium chloride	90

It will be seen that over a large range of concentration the curves are straight, especially in the case of the non-electrolytes. The depression for electrolytes is much greater than for non-electrolytes at the same temperature. This is what was to be expected, owing to the ionisation of the electrolytes in aqueous solution, but the depression is greater than that expected even if the electrolyte were completely ionised. For example, comparing the curve for urea at 70° C. (curve ii) with that for calcium chloride at 70° C. (curve x), it will be seen that, for solutions of equal concentration, the depression in the case of calcium chloride is much greater than in the case of urea. If the greater depression were due simply to the ionisation it should be exactly three times as great, if the calcium chloride were completely ionised. But that is probably not the case in solutions of great concentration. Thus at the concentration denoted by 100 in the diagram, the solution contained 255 grams of the hexadydrate $CaCl_2,6H_2O$ dissolved in 87 grams of water. It is not conceivable that the calcium chloride is completely ionised at such a high concentration, and yet the depression is eight times that produced by a solution of urea of the same concentration at the same temperature (70° C.). Clearly, then, this effect is not due entirely to ionisation. Similarly, but to a less extent, the depression produced by a solution of potassium chloride is more than twice that produced by a solution of urea.

Again, in the case of the non-electrolytes glycerol, cane-sugar, and raffinose, the curves lie above the curve for urea at the same temperature. There is no ionisation in these cases, and the curves should coincide. The depression produced by glycerol and cane-sugar is about half as great again as that produced by a solution of urea of the same concentration, while in the case of raffinose it is about twice as great.

The explanation offered to account for these facts is that most of the solutes form hydrates in solution. In that case, some of the solvent becomes "fixed"; hence the solution is really more concentrated than it is apparently, and so the depression produced by a solution of a substance which forms a hydrate would be greater than that produced by an equally concentrated solution of a substance which does not form a hydrate. The existence of hydrates in solution is supported by the results of many other workers, notably Jones,* Smits,† Biltz,‡ Philip,§ &c.

At the highest concentrations the curve tends to become less steep in the case of calcium chloride and potassium chloride. This is taken to be due to decrease of hydration as well as of ionisation.

* *Amer. Chem. Journ.*, 1905, **34**, 290, &c. † *Zeits. Phys. Chem.*, 1902, **39**, 385.
‡ Ibid. 1902, **40**, 217 ; 1903, **43**, 41. § *Journ. Chem. Soc.*, 1907, **91**, 711.

Some confirmation of these results is afforded by the work of Gerlach.*

He determined the vapour-pressures of solutions of glycerol at 100° C., and the range of concentration varied from 100 per cent. water to 100 per cent. glycerol. A curve showing the relationship between the concentration

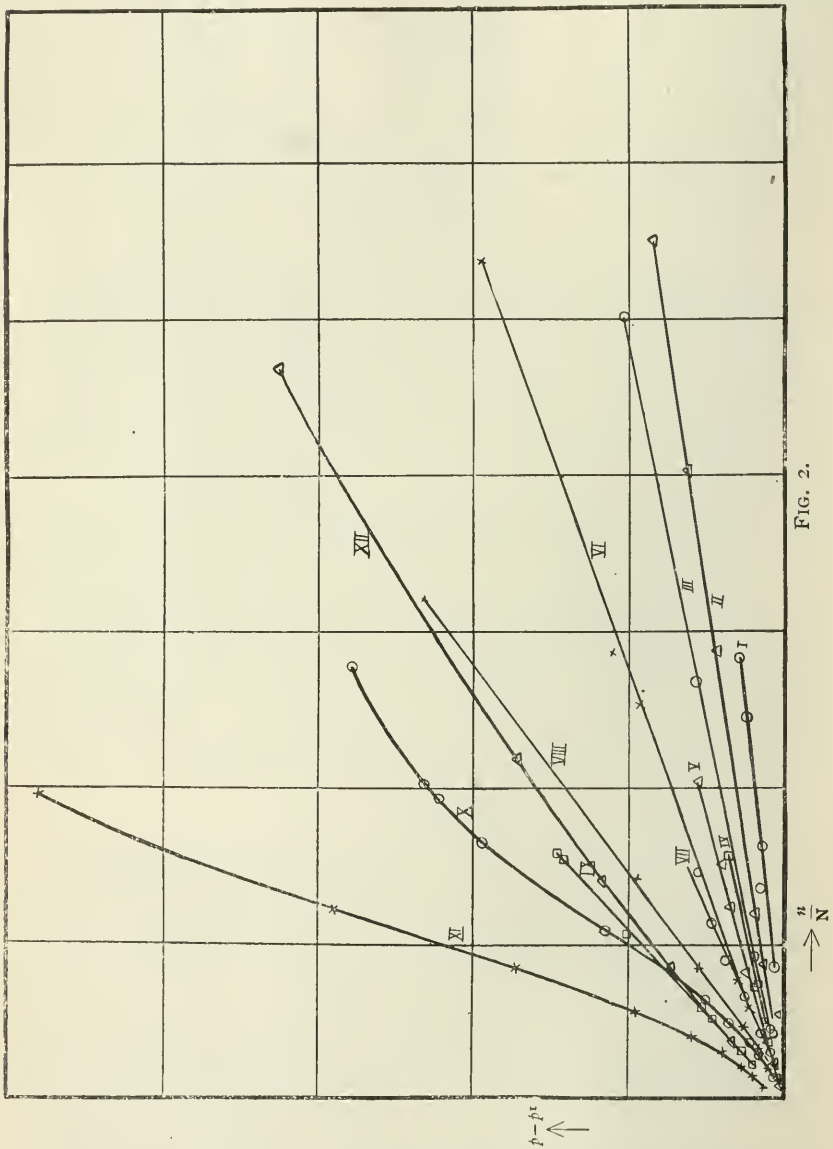


FIG. 2.

and the depression of vapour-pressure has been drawn for this substance at this temperature using Gerlach's figures, and is shown in Fig. 2 (curve xii). The general form is the same as that of our curve for glycerol at 70° C., and both curves become less steep as the concentration increases.

The hydration factor a has been calculated in all cases according to the

* *Chem. Cent.*, 1884 ; *Chem. Ind.*, 7, 277.

formula proposed by Callendar. In the case of urea it is in all cases negative, while in the cases of the other non-electrolytes it is sometimes positive and sometimes negative, and in no case is it a constant. In the case of electrolytes, except potassium chloride at 70° C., where it is negative for dilute solution, a is positive, but decreases gradually as the solution becomes more concentrated. This shows that it is not a constant for any substance, but it appears to be a function of the concentration, as stated by Jones and Bassett (*vide infra*). We do not attach much importance to the values of a calculated for dilute solutions. Co-aggregation of the water molecules or the salt molecules would also affect the result, but we have made no calculations from that point of view.

Babo* found the vapour-pressure of solutions always proportional to that of pure water.

If the vapour-pressure of the solution $= p^1$
" " " water $= p$
Then $p^1 = C.p$ (C = constant)
$p - p^1 =$ lowering of vapour-pressure
Then $p - p^1 = K.p$ when $K = 1 - C$

$$\therefore K = \frac{p - p_1}{p}.$$

Wüllner, Pauchin, Tammann, and Helmholtz† did not confirm Babo's law, although the differences were not great, but they did not agree among themselves.

This law has been tested by means of the figures obtained in the present work. A certain concentration was taken, and the depression of vapour-pressure read from the curves for a substance at two different temperatures. This was repeated at three or four different parts of the curve.

The figures for glycerol at 100° C. were taken from Gerlach.

It will be seen that K is more nearly a constant at the high concentrations than at the low ones. This is due to the greater percentage error in reading the depression from the curve at low concentrations.

In the cases of urea, potassium chloride, and calcium chloride the agreement is good, but not so good in the cases of cane-sugar and glycerol. Thus the law holds with approximate accuracy, and the relative lowering of vapour-pressure is the same for a solution of a particular concentration at different temperatures.

The molecular weights of the substances in aqueous solution have been calculated, and are shown. They were calculated from the formula $M = \frac{p^1}{p - p^1} \cdot \frac{18w}{W}$ where w is the weight of solute, W the weight of solvent, 18 the molecular weight of the solvent (water), p the vapour-pressure of the pure solvent. In all cases the molecular weights calculated from the diminution of vapour-pressure vary greatly from the theoretical. They decrease gradually as the solution becomes more concentrated, which is in accord with the results of Kahlenburg, using the freezing-point and boiling-point methods,‡ and of Krauskopf, using the vapour-pressure method.§ According to the theory of electrolytic dissociation the molecular weights of electrolytes should increase as the solution becomes more concentrated, on account of the decrease of ionisation. But our results are the opposite. In the case of calcium chloride the decrease is very marked, and the molecular weight falls as low as 7. Hence it appears that the formula for calculating molecular weights by means of the depression of vapour-pressure is not applicable to concentrated solutions.

* *Ber. d. Gess. Zur Beförd der Natur. Freiburg.*
† *Wied. Ann.*, 1886, **27**, 568.
‡ *Journ. Phys. Chem.*, 1901, **5**, 339.
§ Ibid. 1910, **14**, 489.

[*Continued on p.* 81.

APPENDIX.

Experimental Data.

In the following data W represents the weight of water absorbed, P the pressure in the last bulb, p the pressure in the aspirator, T the temperature of the aspirator, and V the volume in litres of air drawn through. The concentration is denoted by $\frac{n}{N}$, the ratio of the molecules of solute and solvent. The exact temperature of the bath is given in the left-hand column. The vapour-pressures are corrected to the temperature at the head of each table. a is the hydration factor and M the molecular weight, both calculated from the mean vapour-pressure of each solution.

Temperature of Solution.	P.	V.	W.	T.	p.	Vapour Pressure.	a.	M.	$\frac{n}{N}$	Grams per 100 c.c. Solution.
						Urea at 60° C. Theoretical Molecular Weight = 60.				
°C.	mm.		Grams.	°A.	mm.	mm.				
						146·1*	— 25·87	139·4	0·0512	14·86
60·00	752·0	2·005	0·3446	285·8	738·9	140·5	— 3·76	78·4	0·0819	22·24
60·00	759·6	2·006	0·3434	286·1	746·3	140·5				
						141·4*	— 7·61	104·6	0·0977	25·67
60·03	754·9	2·006	0·3254	285·5	742·1	133·8	— 1·80	104·0	0·1464	34·99
60·02	754·0	2·048	0·3316	285·9	740·9	133·8				
						132·0*	— 1·72	77·5	0·1695	38·85
						Urea at 70° C.				
69·84	735·3	2·004	0·6711	284·1	723·3	231·4	— 105·28	262·0	0·0320	9·65
70·08	741·7	2·005	0·6774	284·9	727·2	232·1				
70·02	767·2	2·003	0·6549	280·5	758·4	226·0	— 19·48	89·1	0·0513	14·79
70·01	762·9	2·003	0·6553	280·5	753·1	226·0				
70·08	764·7	2·003	0·6366	282·6	751·7	223·4	— 6·77	88·8	0·0710	19·61
70·14	749·3	2·003	0·6430	283·4	736·3	222·9				

69·91	741·9	2·003	0·5871	283·4	735·9	209·1	— 2·72	88·0	0·1719	38·95
70·04	744·8	2·003	0·5883	283·3	732·9	209·5				
70·04	771·6	2·004	0·5290	283·0	759·6	195·4	— 1·06	75·5	0·2415	48·71
70·03	768·2	2·003	0·5428	280·0	758·7	197·1				
70·04	753·0	2·004	0·4909	282·7	742·5	183·2	— 0·63	72·4	0·3300	58·45
70·05	769·6	2·003	0·4931	282·9	763·4	184·1				

Urea at 90° C.

89·74	759·5	1·000	1·5040	288·2	744·6	512·3	— 8·67	77·6	0·0341	10·11
89·84	759·5	1·000	1·4780	288·6	743·2	508·0	— 6·74	78·5	0·0458	13·22
89·85	754·3	1·000	1·2050	288·4	738·7	469·7	— 3·77	76·7	0·1519	35·25
89·62	755·0	1·000	1·1764	288·4	737·9	470·2				
90·00	762·6	1·002	1·1547	285·8	750·0	459·76	— 1·13	75·0	0·1717	38·44
90·00	762·1	1·002	1·1510	286·2	747·7	459·69				
90·14	732·5	1·002	0·9313	287·7	716·95	410·55	— 0·44	68·4	0·3227	56·89
89·89	744·65	1·002	0·8897	287·3	729·4	409·81				

Cane-sugar at 70° C. Theoretical Molecular Weight = 342.

70·14	768·0	2·003	0·6698	280·6	758·7	228·6	— 8·26	430·9	0·0280	38·97
70·14	755·3	2·003	0·6644	282·2	744·6	227·4	— 0·41	345·2	0·0285	39·46
70·10	736·1	2·002	0·6502	283·4	725·1	223·5	+ 1·49	320·0	0·0431	52·55
69·97	750·7	2·003	0·6498	281·1	740·6	224·4	— 0·46	348·5	0·0436	52·90
70·07	739·3	2·005	0·6167	279·7	730·9	213·2	+ 0·42	328·8	0·0933	82·61
70·09	745·5	2·003	0·6189	279·6	736·2	213·0				

Cane-sugar at 90° C.

90·04	754·7	1·002	1·6224	292·6	734·1	521·13	— 12·54	393·5	0·0120	19·33
90·00	755·2	1·022	1·6447	292·7	734·6	520·41				
90·03	755·9	1·002	1·5724	292·3	733·1	516·30	— 3·57	365·9	0·0196	29·28
90·03	755·4	1·002	1·5806	292·1	734·8	516·36				

* Determined by Static Method.

EXPERIMENTAL DATA—*continued.*

Temperature of Solution.	P.	V.	W.	T.	t.	Vapour Pressure.	a.	M.	$\frac{n}{N}$	Grams per 100 c.c. Solution.
°C.	mm.		Grams.	°A.	mm.	mm.				
90·04	757·8	1·002	1·5124	292·1	738·7	509·61	— 2·84	314·4	0·0281	38·71
90·02	758·3	1·002	1·5163	292·2	738·6	510·83				
90·00	755·35	1·002	1·3880	290·4	737·45	493·62	4·38	266·3	0·0504	57·99
90·01	755·05	1·002	1·3928	290·6	737·1	494·02				
90·00	756·55	1·002	1 2034	290·3	738·75	469·07	3·49	240·8	0·0847	77·71
90·00	757·65	1·002	1 2026	290·4	738·75	469·69				
90·00	759·35	1·002	0 7694	290·85	741·0	387·48	2·40	183·6	0·1928	—
90·00	754·65	1·002	0·7678	291·35	735·8	386·25				

Glycerol at 70° C. Theoretical Molecular Weight = 92.

69·99	755·6	2·003	0·6586	285·2	744·4	229·3	— 41·00	189·6	0·0259	11·74
69·95	748·0	2·003	0·6724	285·2	736·3	232·5				
69·92	737·8	2·003	0·6600	285·3	725·1	229·1	— 14·01	126·3	0·0266	12·04
69·97	740·6	2·017	0·6610	286·0	727·4	229·6				
69·95	752·0	2·005	0·6286	285·3	738·8	222·4	— 0·92	96·4	0·0540	22·21
69·99	754·1	2·027	0·6384	284·4	741·5	222·3				
70·04	735·7	2·004	0·5516	285·2	723·0	200·4	— 0·35	86·9	0·1602	48·96
70·04	735·2	2·003	0·5478	285·2	722·5	199·4				
70·01	744·8	2·030	0·4562	285·5	731·9	173·1	0·37	81·4	0·3079	68·85
70·00	745·4	2·003	0·4524	285·3	732·7	173·8				
70·00	770·2	2·006	0·3092	283·7	757·6	128·1	0·28	74·7	0·6694	90·18
70·00	770·4	2·005	0·3092	283·7	757·7	128·2				
70·00	768·8	2·003	0·1801	283·8	756·1	80·3	0·15	71·0	1·4390	105·71
69·99	764·9	2·015	0·1792	283·0	752·7	79·3				

Potassium Chloride at 70° C. Theoretical Molecular Weight = 74·5.

69·95	760·3	2·003	0·6437	290·6	740·2	231·4	— 9·55	83·2	0·0123	4·89
69·95	759·8	2·003	0·6428	291·5	741·8	231·1				
70·00	760·8	2·003	0·6483	288·8	745·3	230·0	— 1·07	76·0	0·0186	7·33
70·00	760·3	2·003	0·6480	287·8	745·2	229·3				
70·00	760·4	2·003	0·6233	291·4	743·0	225·6	13·76	48·7	0·0251	9·77
69·97	760·4	2·003	0·6180	291·6	742·8	224·7				
70·00	758·8	2·003	0·5928	291·9	740·4	218·1	11·36	41·9	0·0385	14·66
70·03	760·8	2·003	0·6024	290·7	743·6	219·8				
70·00	759·8	2·003	0·5693	290·9	742·4	211·2	9·46	37·2	0·0525	19·52
70·00	760·3	2·003	0·5756	290·2	744·0	212·2				
70·00	759·8	2·003	0·5521	289·5	743·7	205·6	7·34	37·2	0·0677	24·55
70·05	760·3	2·003	0·5574	289·6	744·6	206·5				
70·00	760·3	2·003	0·5413	288·6	744·5	201·6	5·13	38·6	0·0876	29·53
70·00	759·3	2·003	0·5377	289·5	742·7	201·7				

Potassium Chloride at 90° C.

90·00	753·0	1·002	1·6296	284·3	740·4	514·2	35·82	41·6	0·0123	4·18
90·03	753·3	1·002	1·6314	284·5	740·1	514·7				
90·00	753·8	1·002	1·5890	282·8	742·7	509·65	22·05	43·9	0·0186	7·23
90·00	752·4	1·002	1·5912	283·5	740·9	509·76				
89·96	754·0	1·000	1·4300	289·0	738·4	497·86	14·86	40·9	0·0303	11·58
90·00	743·6	1·000	1·4785	289·7	727·4	498·70				
89·99	751·1	1·000	1·4045	288·4	736·0	494·3	13·04	40·7	0·0348	13·19
89·96	763·2	1·000	1·1546	288·9	747·2	463·8	8·10	36·2	0·0634	22·94
89·92	758·0	1·000	1·1780	289·1	741·8	466·4				
90·02	748·2	1·000	1·0630	288·6	732·9	442·16	5·69	35·5	0·0919	31·76
90·04	751·7	1·000	1·0370	288·8	732·2	439·60				
89·92	750·3	1·000	1·0165	287·9	724·1	438·68	5·60	35·3	0·0939	32·39
89·99	750·2	1·000	1·0240	288·9	732·7	438·83				

EXPERIMENTAL DATA—*continued.*

Temperature of Solution.	P.	V.	W.	T.	*f*.	Vapour Pressure	*a*.	M.	$\frac{n}{N}$	Grams per 100 c.c. Solution.
				Calcium Chloride at 70° C. Theoretical Molecular Weight = 111.						
C.	mm.		Grams.	°A.	mm.	mm.				
70·00	763·7	2·003	0·6665	283·9	751·9	231·2	23·34	87·8	0·0085	5·01
70·02	760·4	2·003	0·6738	282·1	749·1	231·3				
70·00	758·2	2·003	0·6430	287·7	743·15	227·8	36·68	55·7	0·0128	7·62
70·00	758·5	2·003	0·6433	288·0	734·2	228·1				
70·00	753·9	2·003	0·6314	287·6	738·4	224·6	33·95	47·2	0·0169	9·97
70·00	754·3	2·003	0·6305	288·6	738·0	225·1				
70·00	758·7	2·003	0·6188	286·4	744·2	221·0	28·41	42·4	0·0215	12·47
70·00	755·2	2·003	0·6214	287·3	739·9	222·0				
70·00	736·1	2·003	0·5942	286·3	721·6	212·8	23·54	33·3	0·0297	17·22
70·00	731·5	2·003	0·5950	286·3	717·0	212·7				
70·00	738·9	2·003	0·5545	288·5	722·2	204·1	19·82	28·2	0·0376	21·51
70·00	745·2	2·003	0·5531	287·0	730·2	203·3				
70·00	742·8	2·003	0·4236	286·0	728·1	165·6	12·87	17·6	0·0653	35·98
70·00	745·7	2·003	0·4246	284·9	732·2	165·4				
70·00	733·0	2·003	0·2821	285·35	719·2	118·6	9·14	11·1	0·0985	50·76
69·96	744·6	2·003	0·2757	285·5	730·2	117·0				
69·95	752·45	2·003	0·2268	286·0	736·2	99·3	7·87	9·6	0·1161	57·76
70·00	760·0	2·003	0·2296	284·3	744·9	99·8				
69·90	747·3	2·003	0·2134	284·8	733·9	93·8	7·59	9·1	0·1210	58·96
70·00	750·0	2·003	0·2152	286·9	738·1	94·6				
70·00	730·2	2·003	0·1459	286·5	715·6	66·9	5·61	7·3	0·1666*	80·15
70·00	740·3	2·003	0·1409	286·4	722·2	65·1				

Calcium Chloride at 90° C.

90·00	747·7	1·002	1·7164	282·9	736·0	519·48	139·36	39·2	0·0046	2·75
90·00	749·6	1·002	1·6946	283·1	737·8	518·48				
90·00	754·5	1·002	1·6319	283·3	742·6	514·82	65·17	42·4	0·0090	4·95
90·00	754·3	1·002	1·6269	283·6	742·7	514·26				
90·00	756·7	1·002	1·5788	283·1	744·9	510·24	45·94	37·3	0·0125	7·37
90·00	753·6	1·002	1·6017	282·9	741·9	511·06				
89·97	756·2	1·002	1·4955	283·5	744·7	501·68	34·24	42·3	0·0180	10·64
90·00	757·4	1·002	1·4986	283·8	744·7	502·42				
90·00	753·9	1·002	1·4186	283·5	741·4	491·38	28·11	36·9	0·0237	13·69
89·99	734·5	1·002	1·4800	283·5	722·5	490·18				
90·00	737·5	1·002	1·2868	285·0	724·5	468·87	21·93	30·1	0·0332	18·92
90·00	739·65	1·002	1·2683	286·0	725·9	468·13				
90·00	743·5	1·002	0·9668	286·15	730·15	421·26	15·63	22·9	0·0506	27·97
90·00	741·8	1·002	0·9682	286·8	727·5	421·63				
90·00	731·4	1·002	0·6708	286·8	717·1	351·59	11·59	16·5	0·0734	39·06
89·99	729·55	1·011	0·6757	287·0	715·1	351·25				
89·99	735·8	2·003	0·6909	286·7	721·5	236·64	7·66	10·7	0·1178	57·69
90·00	735·5	2·003	0·6929	287·3	720·8	237·43				
90·00	734·0	2·003	0·4103	287·8	718·9	162·12	5·56	8·2	0·1666*	74·12
90·00	741·6	2·003	0·4091	287·7	726·05	162·12				

Raffinose at 70° C. Theoretical Molecular Weight = 504.

70·02	764·3	2·003	0·6728	285·0	751·8	233·41	— 197·47	974·5	0·0047	11·97
70·02	772·7	2·003	0·6746	282·7	761·2	233·06				
70·00	761·9	2·003	0·6608	287·7	747·85	232·35	— 45·53	666·0	0·0074	18·67
70·00	753·4	2·003	0·6642	287·8	738·8	232·59				
70·00	759·3	2·003	0·6607	285·0	746·3	230·35	6·13	463·3	0·0132	29·78
70·00	760·35	2·003	0·6607	285·3	747·1	230·65				
70·00	751·6	2·003	0·6529	286·2	737·7	228·63	1·52	487·1	0·0220	43·80
70·00	751·6	2·003	0·6494	287·3	736·9	228·57				

* Fused hexahydrate.

EXPERIMENTAL DATA—*continued.*

Temperature of Solution.	P.	V.	W.	T.	p.	Vapour Pressure.	a.	M.	$\frac{n}{N}$	Grams per 100 c.c. Solution.
°C.	mm.		Grams.	°A.	mm.	mm.				
70·00	756·4	2·003	0·6324	289·25	740·05	226·19	8·35	393·1	0·0263	53·49
70·00	756·3	2·003	0·6321	289·3	739·9	226·15				
70·00	743·9	2·003	0·6194	288·2	728·9	221·00	5·95	371·3	0·0442	68·87
70·00	764·3	2·003	0·6123	287·0	749·8	220·12				
70·00	762·1	2·003	0·6149	284·6	749·8	218·82	6·26	328·5	0·0482	72·06
70·00	761·9	2·003	0·6125	285·2	749·2	218·60				
70·00	757·3	2·003	0·5926	284·6	744·5	212·82	3·30	363·1	0·0745	88·49
70·00	754·5	2·003	0·5915	285·2	741·3	212·76				
70·00	746·5	2·003	0·5895	283·2	735·15	210·20	2·06	410·4	0·0902	95·51
70·00	746·0	2·003	0·5890	284·0	733·1	210·77				
70·00	749·6	2·003	0·5487	283·9	737·3	200·30	2·13	469·3	0·1221	107·01
70·00	750·9	2·003	0·5522	283·15	738·0	201·05				

WATER OF CRYSTALLISATION IN RAFFINOSE.

The number of molecules of water of crystallisation in raffinose was determined, with the following results:—

Experiment A—Per cent. H_2O ... ... = 15·18
Experiment B—Per cent. H_2O ... ... = 15·02
Mean ... ... = 15·10

This confirms the formula $C_{18}H_{32}O_{16},5H_2O$, the percentage of water in which is 15·15.

UNIVERSITY COLLEGE,
CARDIFF.

We now intend to determine the densities and compressibilities of these solutions, in order to calculate their osmotic pressures.

In conclusion, our best thanks are due to Miss N. D. O'Flyn, B.Sc., for help in some of the earlier experiments, and to the Research Fund, University of Wales, for a grant towards the expenses of the research.

RESULTS.

Substance.	Concentration.	Temperature, °C.	$f-f^1$. mm.	K.
Urea	0·32	70	48	0·2053
	,,	90	110	0·2092
	0 22	70	33·2	0·1420
	,,	90	75·5	0·1436
	0·12	70	18	0·0769
	,,	90	42	0·0798
	0·06	70	9	0·0385
	,,	90	22	0·0418
Cane-sugar... ...	0·092	70	20·5	0·0877
	,,	90	63·5	0·1207
	0·06	70	13	0·0556
	,,	90	40	0·0760
Potassium Chloride	0·092	70	38	0·1625
	,,	90	85	0·1616
	0·06	70	24	0·1027
	,,	90	54·5	0·1036
	0·03	70	11	0·0470
	,,	90	27	0·0513
Calcium Chloride...	0·12	70	137	0·5859
	,,	90	295	0·5610
	0·08	70	90	0·3806
	,,	90	193	0·3670
	0·05	70	46	0·1967
	,,	90	103	0·1958
	0·02	70	11	0·0470
	,,	90	26	0·0494
Glycerol	0·28	70	57·4	0·2459
	,,	100	195	0·2566
	0·2	70	41	0·1753
	,,	100	148	0·1947
	0·1	70	21	0·0898
	,,	100	82	0·1079
	0·05	70	10	0·0428
	,,	100	43	0·0565

SUMMARY.

1. Measurements have been made of the vapour-pressures of solutions of urea, glycerol, cane-sugar, potassium chloride, calcium chloride, and raffinose over a very wide range of concentrations, and at different temperatures.

2. The lowering of the vapour-pressure has been found to be proportional to the concentration, except for very high concentrations.

3. Babo's law has been found to hold in some cases.

4. Hydration, when present, is not fixed, but is a function of the concentration.

DISCUSSION.

Professor A. W. Porter, F.R.S. : I wish to call attention to a discrepancy between the values given for K in connection with Babo's formula and the values that would be expected when the conditions under which Babo's formula holds are considered. Regarding Kirchhoff's equation—

$$\text{Heat of dilution} = RT^2 \frac{\partial}{\partial T}\left(\log \frac{p}{p'}\right)$$

Babo's formula would require the heat of dilution to be zero. Now in the case of sugar this heat is very small, while in that of $CaCl_2$ it is not so. Consequently we would expect Babo's law to hold more closely in the case of sugar than in that of $CaCl_2$; yet Dr. Perman's results indicate the reverse. [When the derivation of the above formula is examined it is easily seen that if R varies with temperature it ought to be placed within the term to which the differential sign applies. Now R varies inversely as the molecular weight of water vapour; consequently the smallness of the heat of dilution implies in reality that $\frac{\log (p/p')}{M}$ does not change with the temperature, where M is the molecular weight of water vapour. To fit in with Dr. Perman's results, M would need to *increase* with the temperature; but, although we have little certain knowledge in regard to the degree of association of water vapour, an increase with temperature is very highly improbable.] Considerations such as these require to be paid attention to in any criticism which the authors' work receives. [Some experiments made for me by Mr. D. Orson Wood since the paper was read indicate that Dr. Perman's results for sugar are erroneous; values obtained at 90° and 70° (the same temperatures as in the paper under discussion) for a nearly concentrated solution satisfy Babo's law. These results must be regarded only as provisional ones and are being repeated and extended with greater elaboration. But so far as they go they raise doubts as to the suitability of the dynamical method of obtaining vapour-pressures: at any rate when used for such viscous solutions as these concentrated ones are apt to be.]

I desire further to protest against the growing practice of expressing concentrations as the number of grams (or molecules) of solute per 100 grams (or molecules) of pure solvent instead of in the old-fashioned way as the number of grams of solute per 100 c.c. (or per 1,000 c.c. or per litre) of solution. The temptation to adopt the newer way arises from the fact that in many cases the curves that arise are straighter than when the old way is employed.

This is no doubt a distinct gain, especially when the slope of the curve for great dilutions has some special physical significance. The reason of my protest is that the new way breaks away from the analogies with the gaseous laws exhibited by fluids and thus introduces confusion into the theoretical interpretation of experimental results. It is sometimes thought (and said) that the new way is equivalent to allowing for *b* (the volume of the molecules of solute) in van der Waals' formula; but in general this is not so, although the allowance is in the right direction. Since, in general, the allowance is only partial, any curvature of the curves obtained has an uncertain meaning. *It may in any particular case be removed if a complete allowance for the* b *term is made.*

I suggest that it will add greatly to the value of the paper if concentrations in the old style be added to those already specified—leaving these latter in for those who may prefer them; and I suggest that it would be well if authors in

general were to adopt this rule of double specification, so as to increase the utility of their work. To change from one mode to the other a table of densities is required.

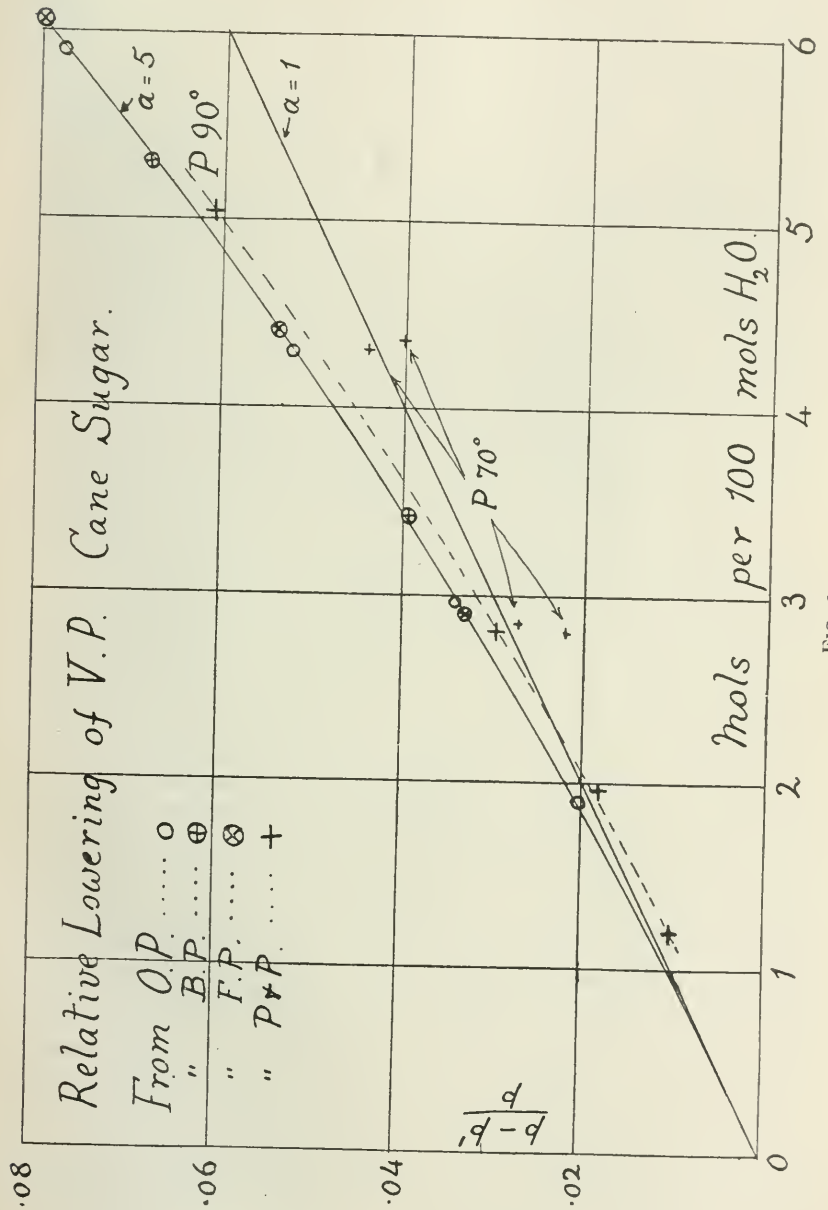


FIG. 3.

Professor H. L. Callendar, F.R.S., wrote that he regretted that he was unable to be present at the discussion, more especially as his theory of the vapour-pressure of solutions had been controverted. The difficulty of obtaining direct measurements of the vapour-pressure of strong solutions was

undoubtedly considerable. Such measurements were of great importance in the theory of solutions, but were at present extremely conflicting, and varied to an almost incredible extent according to the method employed. The authors' results were in many respects superior to those given by some of the older methods, but the values obtained for low concentrations were not sufficiently exact for the purpose to which they had been applied, and those for high concentrations were too widely separated to be of much use in framing a theory to account for the phenomena. He regretted that he was unable to agree with the authors' method of calculating the "hydration factor," and with the conclusions they had drawn from the values obtained. In his opinion the value of the experimental evidence could be estimated in a more satisfactory manner by plotting the concentration n/N against the relative lowering $(p - p^1)/p$ in place of the actual depression $(p - p^1)$ of the vapour-pressure. In order to avoid undue length, he would confine his remarks to the case of cane-sugar, the results for which were plotted in the annexed Fig. 3 on a scale which permitted the experimental errors to be detected. The great objection to direct measurements of the vapour-pressure, which the authors themselves fully appreciated, was that the required depression of the vapour-pressure was obtained as a small difference between large quantities which could not be observed with a high order of accuracy. The indirect measurements of vapour-pressure, depending on the observation of the rise of the boiling-point, or the depression of the freezing-point, or the osmotic pressure, had the advantage that the quantities observed depended directly on the relative lowering or depression of the vapour-pressure, which could be deduced with much greater accuracy on this account, provided that correct methods of calculation were employed in place of the approximate formulæ of van't Hoff, which were inapplicable to strong solutions.

Observations of the rise of the boiling-point and the depression of the freezing-point by a number of different observers had shown that Babo's law (that the relative lowering of the vapour-pressure was independent of the temperature for the same solution) was very accurately followed by solutions of indifferent substances, such as cane-sugar, for which the heat of dilution was negligible. This result was fully confirmed by theory, and could be employed as a test of experimental accuracy. The points shown in Fig. 3 for the relative lowering of the vapour-pressure had been deduced * (1) from the observations of Kahlenberg on the rise of the boiling-point, (2) from the observations of Jones and Getman on the depression of the freezing-point, (3) from the observations of Lord Berkeley on the osmotic pressure. All of these agreed perfectly with the value of the hydration factor $a = 5$ for cane-sugar in the formula which he had proposed for the relative lowering of the vapour-pressure, namely $(p - p^1)/p = n/(N - an + n)$, which followed directly from the law of vapour-pressures for simple mixtures. The observations of Perman and Price at 90° C. followed a nearly parallel curve, shown dotted in the figure, which suggested that their observations of the vapour-pressure were affected by a constant error of about 1 mm. in excess, giving an error of 1 mm. in defect in the depression of the vapour-pressure. Since the whole vapour-pressure observed was about 500 mm., an error of only 1 mm. represented a remarkably high order of accuracy, considering the difficulty of such measurements. A constant error in this direction would naturally follow from the assumption that steam behaves as an ideal gas, which is not accurately true at so high a pressure. The close agreement of the observations of Perman and Price with the curve $a = 5$, was really a very strong confirmation of the hydrate theory, and yet this minute constant error of

* Callendar, *Proc. Roy. Soc.*, A, vol. 80, p. 466.

1 mm., according to their method of calculation, gave values for a varying all the way from $-12{\cdot}54$ to $+4{\cdot}38$. Unfortunately, their values of the vapour-pressure at 70° C. were affected by errors amounting to nearly 1 per cent., but these disagreed among themselves, and indicated that their method was less accurate, as one would naturally expect, at lower temperatures.

Observing the discrepancies in the observations at 70° C., as plotted in Fig. 3, which amounted to 20 per cent. of the depression of vapour-pressure at $100n/N = 2{\cdot}8$, it was not surprising that the authors' observations on cane-sugar did not satisfy Babo's law even approximately. Beyond a concentration of about 7 molecules per 100 of water, the writer had pointed out (*loc. cit.*) that it was probable that lower hydrates were formed, as was known to be the case, but the few sporadic observations available did not suffice to indicate the manner in which the law changed. The hydration theory could not be applied at present with any certainty to strong solutions of electrolytes, owing to want of experimental data for the ionisation and to the wide discrepancies between different observers and different methods. The theory of Jones and Bassett, to which allusion had been made, was merely equivalent to the admission that no definite relation between the hydration and the vapour-pressure was indicated by their observations, when reduced according to their method by approximate formulæ involving serious errors when applied to strong solutions. Many of their data, when correctly reduced, gave very good agreement with the writer's theory. It was out of the question to discuss the whole of the authors' observations in the limits of the present communication, but enough had probably been said to show that their general conclusions must be accepted with considerable reserve.

Dr. E. P. Perman (*communicated reply*): In reply to Professor Callendar and Professor Porter we admit that the accuracy of our results still leaves something to be desired, but we believe that they are the most accurate yet obtained for very concentrated solutions. The statical method will give much greater errors owing to the difficulty of expelling and excluding air from the solutions; one of us has had great experience with both methods. The viscosity of the solutions was never so great as to prevent them from being poured readily from the bulbs when warm.

We have added the concentrations expressed in grams of solute to 100 c.c. solution, as suggested by Professor Porter.

The values of the hydration factor have been calculated directly from Professor Callendar's formula, and we think it of interest to give them throughout, although we have pointed out in our paper that for the more dilute solutions they have not much significance. As Professor Callendar admits the existence of lower hydrates in the more concentrated solutions, there does not appear to be much difference in our views of the question. We have no doubt of the general accuracy of our results, and a consideration of the curves shown in Fig. 2 will suggest, if it will not finally settle, many interesting problems.

THE ELIMINATION OF POTENTIAL DUE TO LIQUID CONTACT—PART II.*

A SIMPLE EQUATION FOR THE CALCULATION OF THE DIFFUSION POTENTIAL.

By ALEXANDER CHARLES CUMMING, D.Sc.

(*A Paper read before the Faraday Society, Tuesday, March 26, 1912,*
MR. ALEXANDER SIEMENS, VICE-PRESIDENT, *in the Chair.*)

It has long been known that there is a source of potential at the surface of contact of two solutions, so that the measured potential of a cell is the sum of this contact potential and of the electrode potential difference. The experimental measurement of one of these, independently of the other, is not possible. A simple theory of this diffusion potential was given by Nernst,† who showed also how it could be calculated in certain simple cases.

Planck ‡ deduced a more general expression whereby the diffusion potential could be calculated if all the ions present had the same valency. Planck points out that his formula is only strictly applicable when dissociation is complete, *i.e.*, in very dilute solutions, but Negbaur § obtained very fair agreement in solutions up to decinormal between the calculated and observed values. Planck's formula for the potential difference $(\phi_1 - \phi_2)$ is as follows—

$$(\phi - \phi_2) = \frac{RT}{wF} \log_n \xi$$

where ξ is defined by the equation—

$$\frac{\xi U_1 - U_2}{V_1 - \xi V_2} = \frac{\log_n \frac{c_1}{c_2} - \log_n \xi}{\log_n \frac{c_1}{c_2} + \log_n \xi} \cdot \frac{\xi c_1 - c_2}{c_1 - \xi c_2}$$

w is the valency,
R is the gas constant,
F is the electrochemical unit,
$U_1 = u'c' + u''c'' + \ldots\ldots$
$V_1 = v'c' + v''c'' + \ldots\ldots$

and U_2 and V_2 are the similar sums for the second solution. (The u' and v' symbols represent the ionic mobilities and the c' symbols the corresponding ionic concentrations.) c_1 and c_2 are the total ionic concentrations.

K. R. Johnson || has extended Planck's equation to the case where the anions and cations have different valencies, though all the anions must have

* A previous paper on the elimination of diffusion potential, using a saturated ammonium nitrate solution, appeared in this *Journal*, **2**, 213, 1907.
† *Zeit. Physik. Chem.*, **2**, 613, 1888, and **4**, 129, 1889.
‡ *Wied. Annalen*, **40**, 561, 1890.
§ *Ibid.*, **44**, 737, 1891.
|| *Annalen der Physik*, **14**, 995, 1904.

the same valency, and similarly all the cations must have the same valency. The equation is even more complicated than that of Planck.

Both of these equations are expressions for the potential when there is a sharp boundary between the two solutions. If two liquids are brought into contact in such a way as to give a sharp boundary there will be diffusion from each solution into the other. If mixture takes place by diffusion alone the concentration in any layer is determined by two independent variables, the rates of diffusion of the salts. In general, therefore, the concentration in any layer after diffusion has proceeded for some time will not be the same as would be obtained by mixing the two solutions.

If instead of a sharp boundary the solutions are mechanically mixed at the boundary, the connecting layer may be regarded as a series of mixture of the two solutions in all proportions. P. Henderson* has investigated this problem and shown (1) that it is mathematically much simpler than that studied by Planck, leading to a much simpler equation, and (2) that it corresponds to a state which is more easily realised experimentally than that postulated by Planck. Henderson's equation is easy to apply in practice and is also the only equation which is applicable to cases where the radicals have different valencies, without restriction of any kind. The diffusion potential, E, is obtained from the equation—

$$E = \frac{RT}{F} \cdot \frac{(U_1 - V_1) - (U_2 - V_2)}{(U'_1 + V'_1) - (U'_2 + V'_2)} \log_n \frac{U'_1 + V'_1}{U'_2 + V'_2}$$

where in the one solution—

$$U_1 = u_1c_1 + u_2c_2 + u_3c_3 \ldots\ldots$$
$$V_1 = v_1c'_1 + v_2c'_2 + v_3c'_3 \ldots\ldots$$
$$U'_1 = u_1c_1w_1 + u_2c_2w_2 + u_3c_3w_3 \ldots\ldots$$
$$V'_1 = v_1c'_1w_1 + v_2c'_2w_2 + u_3c'_3w_3 \ldots\ldots$$

and U_2, V_2, U'_2, and V'_2 represent the corresponding sums in the second solution. The u and v symbols represent the mobilities of the ions, c the equivalent concentration, and w the valency.

Henderson points out that it has been assumed in the deduction of this formula that the fall of concentration from c to zero in the mixed layer is linear, and that this is not strictly true unless the salt is fully dissociated. The error on this account will probably be small for dilute solutions of highly dissociated salts. Henderson does not explicitly state what he uses as the "mobilities" of the ions, and neither in his thesis nor his *Zeitschrift* papers is the temperature at which the experimental work was done mentioned. I find that his calculated values agree with the supposition that the temperature was 18°, and the "mobilities" are the ionic velocities at infinite dilution. Since the mobilities of some ions vary considerably with the concentration, it was thought of interest to modify the Henderson equation by using the mobilities at the corresponding experimental concentrations. It is probable that neither of these assumptions is strictly true, but there seems more justification for taking the ionic velocities at the corresponding concentration.

When this assumption is made a considerable simplification of the Henderson equation is possible for cases when the anion and cation of each salt has the same valency. The equation in this case becomes (for solutions of single salts)—

$$E = \frac{RT}{F} \cdot \frac{c_1(u_1 - v_1) - c_2(u_2 - v_2)}{c_1w_1(u_1 + v_1) - c_2w_2(u_2 + v_2)} \log_n \frac{c_1w_1(u_1 + v_1)}{c_2w_2(u_2 + v_2)}.$$

* Dissertation, Göttingen, 1907 ; *Zeit. Physik. Chem.*, 59, 118, 1906, and 63, 325, 1908.

This can be simplified by expressing it in terms of the specific conductivity κ and the migration ratio n. We have $\kappa = c(u + v)$ and $n = \frac{u}{u+v}$, or $(u - v) = (u + v)(2n - 1)$, so that—

$$E = \frac{RT}{F} \cdot \frac{\kappa(2n - 1) - \kappa'(2n' - 1)}{w_1\kappa - \kappa' w_2} \log_n \frac{\kappa w_1}{\kappa' w_2},$$

where κ and κ' are the specific conductivities, n and n' the migration ratios, and w_1 and w_2 the corresponding valencies. This equation is not so generally applicable as the original Henderson equation, but, on the other hand, it is simpler, and it is expressed in terms of the specific conductivity and migration ratio only, values for both of which are readily accessible in the literature. It differs from the Henderson equation in using the actual mobility at the corresponding concentration instead of the mobility at infinite dilution.

Further Simplification for Special Cases.—For the case of a concentration cell, where there are two solutions of the same salt, the equation becomes identical with that of Nernst for the same case if it is assumed that the migration ratio is the same in the two solutions. In this case the equation becomes—

$$E = \frac{RT}{wF} \cdot (2n - 1) \cdot \log_n \frac{\kappa}{\kappa'},$$

which is identical with Nernst's well-known equation—

$$E = \frac{RT}{wF} \cdot \frac{u - v}{u + v} \cdot \log_n \frac{c_1}{c_2}.$$

If the two concentrations are far apart it is evident that this gives only an approximation. Nernst has himself pointed out that the equation is strictly true only when dissociation is complete, but in practice experiments are rarely, if ever, confined to such dilute solutions.

For the case when the two solutions are of equal ionic concentration, and have one ion in common, the equation becomes (for univalent ions)—

$$E = \frac{RT}{F} \log_n \frac{\mu}{\mu'}$$

where μ and μ' are the equivalent conductivities of the two solutions. This equation has already been deduced for this case by G. N. Lewis and Sargent* from the Planck equation. They obtained it by the same assumption as I have made above, namely, that the actual mobilities at the corresponding concentrations should be used instead of the ionic mobilities at infinite dilution. Planck's equation presupposes that the boundary is sharp, while Henderson's assumes that the two liquids have been mixed at the boundary. At first sight, therefore, it would seem impossible to obtain the same equation in both ways. As Henderson has already pointed out, in this particular case, the concentration gradient at the boundary is the same whether the mixed layer is formed by mechanical mixture of the two solutions or by diffusion. Theoretically therefore both equations should simplify to the same expression in this case.

Comparison of the Equation with Experimental Measurements.—There are abundant data in the literature more or less suitable for checking the above equation, but some appear more trustworthy than others. A first choice was

* *Journal Amer. Chem. Soc.*, 31, 363, 1909.

made of results which appeared likely to be experimentally accurate, and the selection was further restricted to cases where the electrode potential could be calculated without too many assumptions. Apart from this there has not been any discrimination. All the data which have been calculated are included, so that the agreement between the calculated and experimental values is in no way dependent on the omission of results which are not in accord with the theory.

Henderson (*loc. cit.*) gives a series of measurements* of the type—

Hg	HgCl	Solution I. 0·1 Normal	Solution II. 0·05 Normal	HgCl	Hg,

where Solutions I. and II. are chlorides of different metals. In the calculation of the diffusion potential it has been assumed that the temperature of experiment was 18°, and the values used for the specific conductivities and migration ratios are those given in Kohlrausch and Holborn.†

TABLE I.

Solutions.		Electrode Potential calculated by Nernst's Equation.	Calculated Diffusion Potential.	Total Calculated Potential.	Observed Potential (Henderson).	Difference.
$\frac{N}{10}$	$\frac{N}{20}$					
HCl	KCl	0·0181	0·0347	0·0528	0·0518	0·0010
KCl	HCl	0·0151	— 0·0196	— 0·0045	— 0·0046	0·0001
HCl	NaCl	0·0183	0·0384	0·0567	0·0557	0·0010
NaCl	HCl	0·0148	— 0·0265	— 0·0117	— 0·0100	0·0017
HCl	LiCl	0·0186	0·0404	0·0590	0·0575	0·0015
LiCl	HCl	0·0145	— 0·0298	— 0·0153	0·0126	0·0027
KCl	NaCl	0·0169	0·0030	0·0199	0·0191	0·0008
NaCl	KCl	0·0161	— 0·0071	0·0090	0·0094	0·0004
KCl	LiCl	0·0171	0·0045	0·0216	0·0206	0·0010
LiCl	KCl	0·0158	— 0·0108	0·0050	0·0063	0·0013
NaCl	LiCl	0·0169	— 0·0027	0·0142	0·0124	0·0018
LiCl	NaCl	0·0161	— 0·0081	0·0080	0·0092	0·0012

The calculated values differ on the average 1·2 millivolt from the experimental values. In view of this difference it may be as well to consider the various sources of error. Henderson states that two pairs of cells were always prepared and the results rejected if they did not agree to $\frac{1}{10}$ millivolt. This is a very high order of accuracy, and is rarely attained if the materials used are from different sources.

There are several approximations made in the deduction of the diffusion equation, and it is difficult to judge what error these will introduce. Another source of error lies in the uncertainty of the values of the migration ratio, and the divergencies with the lithium chloride cells may be in part due to this cause. One merit of the proposed equation is that it substitutes for $c(u + v)$ a single value κ (the specific conductivity), and should therefore tend to reduce errors due to uncertainties in these three values singly. In the calculation of the electrode potential, it is, however, necessary to use values for the

* In Henderson's thesis the "calculated" and "observed" values in Tables XII. to XVI. are reversed, and the same slip occurs in his other papers.

† *Zeit. der Electrolyte*, 1898.

ionic concentrations. Nernst's equation for the electrode potential difference of a concentration cell is—

$$e = \frac{RT}{F} . \log_n \frac{c_1}{c_2},$$

where c_1 and c_2 are the ionic concentrations. It is usual to assume that the ratio of the conductivities is the same as that of the ionic concentrations, and the values for the electrode potential difference have been calculated on this basis throughout this paper. The difference between the calculated and observed values may therefore be partly due to errors in the calculation of the electrode potential difference. To illustrate the difficulty of obtaining an exact basis for comparison, the available data may be quoted for the cell :—

Hg | HgCl | o·1 HCl | o·1 KCl | HgCl | Hg.

Sauer,* as the mean value for 6 cells at 18°, found the electromotive force to be o·0286 volt. Bjerrum † for the same combination at 25° gives the value as o·0278 volt. If the ionic concentrations are calculated from the conductivities, the electrode potential difference is o·0016 volt on account of the greater dissociation of the acid. Noyes and Sammet ‡ have shown that the mobility of the hydrogen ion increases rapidly with the concentration. If a correction is made for this, HCl and KCl are found to be equally dissociated in decinormal solution, and the electrode potential difference will be *nil*. The following table shows the results for o·1 HCl — o·1 KCl on these different assumptions :—

Table II.

	Electrode Potential Difference.	Calculated Diffusion Potential.	Total Calculated Potential.	Observed Potential.	Difference.
Sauer at 18° ...	o·0016	o·0269	o·0285	o·0286	o·0001
	o·0000	o·0269	o·0269		o·0017
Bjerrum at 25°...	o·0016	o·0276	o·0292	o·0278	o·0014
	o·0000	o·0276	o·0276		o·0002

It is evident that the degree of accord between the calculated and observed values is largely dependent on the choice of data for the calculation. So much is uncertain at present that the agreement shown in Table I. is as close as can be expected.

As already mentioned, Lewis and Sargent have simplified Planck's equation for the special case of two solutions of equal concentration and with a common ion, and obtained the same expression as is given in this case by the equation proposed in this paper. The agreement between their calculated and experimental results is remarkably close, but it is open to criticism on a minor point. The solutions used by them were of equal normality but not of equal ionic concentrations as judged by conductivity measurements. On this account they apply a correction for the electrode potential difference due to the unequal ionic concentrations, but take no account of this difference in the calculation of the diffusion potential. Their

* *Zeit. Physik. Chem.*, **47**, 146, 1904.
† *Zeit. für Electroch.*, **17**, 391, 1911.
‡ *Journal Amer. Chem. Soc.*, **24**, 758, 1902, *and* **25**, 167, 1903.

results have, therefore, been recalculated, and are given in the following table (temperature, 25°) :—

TABLE III.

	Electrode Potential from Nernst's Equation.	Calculated Diffusion Potential.	Total Calculated Potential.	Observed Potential.	Difference.
0·1 KCl—0·1 $KC_2H_3O_2$	0·0006	—0·0080	—0·0074	—0·0074	0·0000
0·2 KCl—0·2 $KC_2H_3O_2$	0·0011	—0·0084	—0·0073	—0·0069	0·0004
0·2 KCl—0·2 KOH	—0·0009	0·0162	0·0153	0·0161	0·0008
0·1 KCl—0·1 KOH	—0·0008	0·0159	0·0151	0·0156	0·0005
0·2 KCl—0·2 KBr	0·0000	0·0004	0·0004	0·0004	0·0000
0·2 NaCl—0·2 NaOH	0·0011	0·0181	0·0192	(0·01 1)	—

The last cell is said to have been less constant than any of the others, the potential being given as 0·0181 ± 0·0003. All values are the mean from at least six measurements, using the ferro-ferricyanide electrodes described by the same investigators.* The conductivities of the solutions have been taken from Lewis and Sargent's paper. The migration ratios used in the calculation are those given by Kohlrausch and Holborn for 18°, but no appreciable error can be introduced by using these values at 25° for such small corrections.

Another series of measurements which are suitable for comparison are given by Bjerrum (*loc. cit.*) who has measured the potential of various chloride solutions with calomel electrodes. His values are of special interest for the present purpose as the experimental conditions were intentionally arranged to give a mixed boundary, adapted to calculation by the Henderson equation. Bjerrum estimates the probable error of the measurements at not more than 0·2 millivolt, but found differences of 0·3 and 0·4 millivolts in some cases, particularly with the more dilute solutions. Two electrodes of each kind were prepared and the value given is the mean. The potential measurements were made at 25°, but the calculated values are from conductivity data at 18°. It is improbable that this introduces any appreciable error, since only the ratios of the conductivities and mobilities are required.

TABLE IV.

Cell Solutions.		Calculated Electrode Potential (Nernst).	Calculated Diffusion Potential.	Sum of Calculated Potentials.	Observed Potential.	Difference.
0·10 HCl	0·10 KCl	—0·0016	—0·0276	—0·0292	—0·0278	0·0014
0·10 NaCl	0·10 KCl	0·0005	0·0050	0·0055	0·0041	0·0014
0·01 HCl	0·10 KCl	0·0562	—0·0101	0·0461	0·0458	0·0003
0·01 HCl	0·10 HCl	0·0577	0·0370	0·0947	0·0935	0·0012
0·01 KCl	0·10 KCl	0·0568	0·0008	0·0576	0·0576	0·0000
0·01 NaCl	0·10 KCl	0·0570	—0·0028	0·0542	0·0553	0·0011
0·01 NaCl	0·01 KCl	0·0002	0·0048	0·0050	0·0039	0·0011
0·09 KCl + 0·01 HCl	0·10 KCl	—0·0002	—0·0050	—0·0052	—0·0041	0·0011
0·10 NaCl	0·09 KC + 0·01 HC	0·0007	0·0097	0·0104	0·0083	0·0021
					Average	0·0011

* *Journ. Amer. Chem. Soc.*, **31**, 355, 1909.

The difference given in the last column represents the aggregate error due to (1) experimental errors in the potential values, (2) errors in the conductivities which are used in the calculations, (3) errors due to the approximations made in the deduction of the diffusion equation, and (4) errors due to using the conductivity data as an estimate of the ionic concentration in the more concentrated solutions. The last error is probably the most serious since it affects the calculated values of both the electrode potential difference and the diffusion potential. At present, therefore, it is impossible to so apportion the difference between the experimental and calculated results as to lead to an estimate of the error in the calculation of the diffusion potential.

Bjerrum has calculated the diffusion potential from Henderson's equation, and if the results are tabulated in the same way as in Table IV., the difference between the observed and total calculated values is 1·5 millivolt (against 1·1 millivolt in the above table). In a previous paper I * recommended a saturated ammonium nitrate solution as a connecting solution to eliminate the diffusion potential. Bjerrum gives figures for nine cells (see Table IV.) with direct connection, and also when connected with saturated ammonium nitrate solution. The potential with direct connection minus the calculated diffusion potential gives the electrode potential difference, and these values should agree with the potentials when the diffusion potential is eliminated by ammonium nitrate. The average divergence is 0·0007 volt. The electrode potential difference can also be calculated directly from Nernst's equation, and this set on comparison with the ammonium nitrate values show also an average divergence of only 0·0007 volt.

Conclusion.

In view of the various sources of uncertainty it may fairly be claimed that the proposed modification of the Henderson equation for certain cases is supported by the experimental evidence. The proposed equation, when more than one salt is present in the same solution, becomes—

$$E = \frac{RT}{F} \cdot \frac{\Sigma\kappa(2n-1) - \Sigma\kappa'(2n'-1)}{\Sigma w_1\kappa - \Sigma\kappa' w_2} \log_n \frac{\Sigma\kappa w_1}{\Sigma\kappa' w_2}.$$

It is not possible to simplify the Henderson equation in a similar manner when the anion and cation of any salt in the system have different valencies.

It may be pointed out that this equation is not only simpler than Henderson's, but it is probably more accurate since it substitutes the mobilities at the experimental concentration for the mobilities at infinite dilution. It presents also the marked advantage that the only data required, namely, the conductivities and the migration ratios, are readily obtained by direct experiment.

A critical review of the present data of our knowledge of electromotive force work indicates, in my opinion, that no electrode potential difference or diffusion potential is known *separately* with a greater accuracy than about 1 millivolt. In many cases it is possible to measure the *total* potential with certainty to $\frac{1}{10}$ millivolt, if not even closer. The problem is, of course, solved if *either* potential can be estimated accurately, and experiments with this aim are at present in progress.

* This *Journal*, **2**, 213, 1907.

The elimination of diffusion potential by the use of various connecting solutions such as saturated ammonium nitrate * and of potassium chloride † can only be justified by comparison with values involving calculations such as have been dealt with in this paper. I hope to deal with the respective merits and demerits of these devices when there is a surer basis of comparison.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF EDINBURGH.

* Cumming, this *Journal*, 2, 213, 1907.
† Bjerrum, *loc. cit.*, and *Zeit. Physik. Chem.*, 53, 428, 1905.

MAGNETIC PROPERTIES OF ALLOYS.

At the Meeting of the Faraday Society held on Tuesday, April 23, 1912, at the Institution of Electrical Engineers, Victoria Embankment, London, W.C., a General Discussion on **Magnetic Properties of Alloys** took place. **Sir Robert Hadfield, F.R.S.**, who was in the chair, prefaced the discussion with the following remarks:—

I have much pleasure in opening this important meeting. It may not be so large as some of the gatherings in this room are, but I think that from the excellent character of the papers which have been submitted it will be agreed that they deal with problems which, so far as I know, no other society in this country or elsewhere has yet attempted to grapple with in the way that is being attempted this evening. We are very pleased to welcome from Germany Geheimrat Dr. Gumlich, Professor Wedekind, Professor Du Bois, and Dr. Hilpert. We in London are always glad to see our friends from Berlin, perhaps specially so this year because of the fact that the Iron and Steel Institute, with which I have been connected for many years, could not find a better recipient or competitor for the Carnegie Gold Medal than Dr. Goerens, of Aachen, and we congratulate you who are present this evening on that distinguished honour.

We are going to take up this evening papers dealing with a very interesting line of research, namely, magnetic phenomena, to which in the past there have been important contributions from Sir William Barrett, Lord Kelvin, M. Dumas in France, Professor Ledebur in Germany, and Dr. Howe and Professor Knowlton in America. In making a few remarks on what we shall deal with this evening, I can only speak from one particular point of view, and that is as regards ferro-alloys. I would say that I believe David Mushet was the first to notice the non-magnetic qualities of the iron-manganese alloy known as Spiegeleisen. It was, however, in 1882 when I commenced my own research work on this important subject, and from that year until 1888 I persevered with the study of the influence of manganese upon iron, producing what is now known as manganese steel, which was the first malleable and practical non-magnetic ferro-alloy to be

made. To those who are interested in this matter I may remark that I have here this evening two specimens exhibited which represent the first manganese steel ever produced; members present may afterwards like to examine them. I read a number of papers on the subject, one on "Manganese Steel" before the Institution of Civil Engineers in 1888, and another paper on "Alloys of Iron, Manganese, and Nickel" before the same Institution; also similar papers to the Iron and Steel Institute, including one on the "Production of Magnetic Alloys from Non-magnetic Metals." Then in conjunction with Dr. Fleming I read a contribution before the Royal Society on the subject of "Magnetic Qualities of some Alloys not containing Iron," also a recent joint paper with Professor Hopkinson, read before the Institution of Electrical Engineers, on "Magnetic Properties of Iron and its Alloys in Intense Fields." There are also various papers on the subject by Barrett, Brown, and myself contributed to the Royal Dublin Society in 1900, 1902, and 1904, and to the Institution of Electrical Engineers in 1902. It will therefore be seen that for many years special attention has been paid to the study of the magnetic and non-magnetic qualities of ferro-alloys. In order to give some idea of the enormous amount of study which the subject of magnetic qualities of ferro and other alloys of iron and steel has received, I may say that at least five hundred papers have appeared on the question of magnetic materials and their properties during the past few years. The subject is therefore one of great interest and has been very much investigated. Although I am a non-allotropist in not agreeing that a hard adamantine β form of iron exists, I think it was my paper in 1888 on "Manganese Steel" which originated this theory, for I said that while I considered that the sole cause of the hardening of manganese steel did not seem to be due to the manganese itself, there might be some change of form in the iron itself, some form not hitherto suspected. Singular to say, Sir William Roberts-Austen, who gave so much attention to the allotropic theory, said he thought I had underrated the influence of the small amount of carbon which the manganese alloy contained; in other words, the carbon present was the determining cause. And I think he was right, but not in the theory which he afterwards took up as to there being a hard adamantine β form of iron. To show the extraordinary nature of this alloy I have brought a very peculiar specimen, namely, a bar of manganese steel which is in one piece, that is, not welded. It is, and has always been, the same bar, no weld or combination of parts. At one end, as you can easily see by the application of the magnet, it is practically non-magnetic; by holding the magnet at the other end it will be seen to be very

magnetic. This, therefore, is a remarkable bar of steel, the change in magnetic conditions being produced by heat treatment, so it shows that with the same product and the same composition you can have magnetic and non-magnetic states or conditions in the same bar. I have also here some manganese steel which contains 18 per cent. of manganese; you will see it is practically non-magnetic. That specimen, remember, contains manganese to the extent of 18 per cent. Here is also an interesting specimen of manganese steel in the sense of containing a large amount of manganese. This material, which contains 5 per cent. of manganese, is so brittle that you can take a piece of it in its cast form and powder it with a small hand hammer almost as easily as sandstone. I have shown you the ordinary manganese steel which is non-magnetic, and I show you a brittle specimen of manganese steel which is magnetic. Take this brittle percentage, 5 per cent., and alloy it with iron and 14 per cent. nickel, and you get a product somewhat of the nature of manganese steel. It is exceedingly tough and can be bent double cold. The brittleness disappears, although there is the same percentage of manganese present as in the specimen just mentioned. Its tensile strength is about 50 tons per square inch, yet, as I have pointed out, there is the same percentage of manganese present as in the product which can be powdered almost like sandstone. That is rather a remarkable combination of elements, and it shows it is impossible to predict the nature of any particular ferro-alloy unless the whole series and combination is carefully worked through; otherwise it is easy to miss the most interesting ones amongst them. Probably the magnetic qualities of the various alloys are not produced by chemical combinations, but even the same combinations may vary according to their physical nature, and perhaps that aspect of the case has much more to do with magnetic qualities than with the composition alone. I would like to call your attention to a very interesting paper in the collection of valuable contributions which are to be presented to us this evening, namely, that by Professor Knowlton. I have been very much struck with his clearness of observation on this very difficult problem. Professor Knowlton I have never met, having only corresponded with him. He is working at the University of Utah in Salt Lake City, and has put forward some excellent explanations, so far as I am able to judge, as to the peculiarities noticed in these various combinations, especially ferro-alloys. As regards the practical value of some of these non-magnetic products, of course if we could build a ship entirely of non-magnetic material we should have no compass variations. But the material is too expensive, and there are practical difficulties in the way of working it. We

are, however, applying these non-magnetic products to many other purposes. Here is a photograph of a rolled rail which was made about seven years ago; the material is used on account of its combination of toughness and hardness. For this particular purpose the non-magnetic qualities of the material are not of special commercial value, but the physical properties of the alloy are very valuable. I will not take up any more of your time now, but will ask Dr. Gumlich to read the first paper.

MAGNETIC PROPERTIES OF IRON-CARBON AND IRON-SILICON ALLOYS.

Professor Dr. E. Gumlich, Member of the Physikalisch-Technische Reichsanstalt, Charlottenburg, then read his Paper on "Magnetic Properties of Iron-Carbon and Iron-Silicon Alloys," with Micrographic Investigation and Reproductions by **Professor D.Ing. P. Goerens,** Docent of the Technische Hochschule, Aachen.

(*Communication from the Physikalisch-Technische Reichsanstalt and the Eisenhüttenmännisches Institut of the Technische Hochschule, Aachen.*)

At the suggestion of German technologists the Physikalisch-Technische Reichsanstalt (P.T.R.) began some years ago to examine the connection between the magnetic properties of iron alloys and their chemical compositions and thermical treatments. The Verband Deutscher Elektrotechniker supported these extensive and expensive researches by the grant of a considerable sum of money, as did also some large ironworks by supplying the necessary samples and chemical analyses. Especially grateful is the P.T.R. to Professor Wüst, Director of the Eisenhüttenmännisches Institut of the Technische Hochschule at Aachen, and to Professor Goerens, for much skilful advice and for microphotographic reproductions of the samples magnetically examined at the P.T.R. The P.T.R. is much obliged for this varied and valuable assistance, without which the accomplishment of the work would hardly have been possible. The results of the experiments have not yet been published ; it was thought best to wait until a definite conclusion had been reached, and that may extend over some years. But because the discussion arranged by the Faraday Society is partly intended to elucidate the same questions as the researches of the P.T.R., the P.T.R. decided at once to place at the disposal of the public those researches which could be of importance to the actual discussion. But we must add that those experiments have not as yet been carried to a conclusion, and that later on some results may have to be corrected more or less, principally on account of the foreign substances included in the samples, the effect of which only then can be taken into exact consideration, when the influence of larger quantities of those substances on the magnetism of the iron will be examined.

I will first refer to the examination of a series of iron-carbon alloys.

In the first analytical table the samples are arranged according to the increasing percentages of carbon. The chemical analysis was made at first by the works which supplied the samples, but was afterwards repeated by the Hoesch Ironworks at Dortmund. The differences between the two analyses were not great in general ; average values are given in Table I. The diagrams, which show the connection between the magnetic properties and the percentage of carbon, are partly attached to the analyses of the works supplying the samples only, but that is of no consequence.

In order to distinguish the samples, those supplied by the Electro-steel-works R. Lindenberg at Remscheid-Hasten are indicated by a point (.) ; the samples of the Steelworks Phönix, Ruhrort, by a St. Andrew's cross (×) ; those of the Steelworks Phönix, Hörde, by a St. George's cross (+). The two first specimens are taken from commercial products, therefore the admixtures of silicon and chiefly of manganese are undesirably large. Only the samples (+) were especially made for the purpose in question of much greater purity. The quantity of phosphorus and sulphur amounts in all samples to a few hundredths per cent. only ; therefore they have not been especially noticed in the analysis.

The magnetic measurements were, in field up to 300 gauss, conducted on rods, 6 mm. in thickness and 18 cm. in length, with the Hopkinson yoke and the ballistic galvanometer. The necessary shearing was approximately known from earlier researches, and was in each case more exactly determined by measuring not only the apparent coercive force yielded by the yoke, but

TABLE I.

Chemical Analysis.

Notation..	Sign.	C.	Mn.	Si.
		Per Cent.	Per Cent.	Per Cent.
C 6	×	0·07	0·48	0·10
C 11	.	0·11	0·25	0·16
C 16	.	0·16	0·35	0·19
C 21	×	0·21	0·52	0·11
C 23	+	0·23	0·18	0·04
C 44	+	0·44	0·13	0·06
C 51	×	0·48	0·52	0·12
C 69	+	0·69	0·13	0·16
C 71	.	0·71	0·29	0·21
C 73	×	0·71	0·51	0·14
C 107	.	0·77	0·26	0·16
C 99	.	0·99	0·25	0·24
C 114	+	1·11	0·13	0·10
C 156	.	1·57	0·37	0·23
C 180	+	1·78	0·17	0·10

also the true coercive force by the magnetometer. That can likewise be quickly and surely done for rods of any shape, and thus a constant is obtained which is extremely important for the characterisation of the magnetic material.

Measurements in strong magnetic fields were made by the isthmus method, which we owe to your ingenious countryman Ewing. In the original arrangement there is placed between the poles of a strong electromagnet a double cone of the material to be examined ; the cone can be turned, and the points are joined by a short and thin rod, the isthmus. The induction is high in the isthmus, and its intensity depends upon the dimensions of the magnet, the form of the cone, the length and the diameter of the isthmus, and so forth. The isthmus is wound with two layers of a fine wire of the same number of turns, the inner of which closely surrounds the isthmus, while the outer is slightly separated from it. If the *inner* coil be joined to a ballistic galvanometer, and the cone be turned through 180 degrees, the deflection of the galvanometer is proportional to the induction in the isthmus. If on the

other hand the two coils be joined in opposition to one another, the deflection of the galvanometer will be proportional to the flux of lines of magnetic force in the annular space between the two coils, which answers to the magnetic field there existing. The two throws of the galvanometer are therefore measuring at the same time the induction and the field belonging to it, if the latter may be regarded as identical for the isthmus and for the annular space.

For practical purposes, this method, with which Ewing made some very interesting measurements in magnetic fields of 24,000 gauss maximum, has certain inconveniences. The principal of these consist in the fact that for each new measurement a complete cone must be prepared ; further, the area of the turns of the coils, which considerably influence the results of the measurements, can only be deduced from the dimensions and therefore not very correctly be determined. Lastly, the method in that form can only be applied to relatively strong fields ; because, owing to the small number of

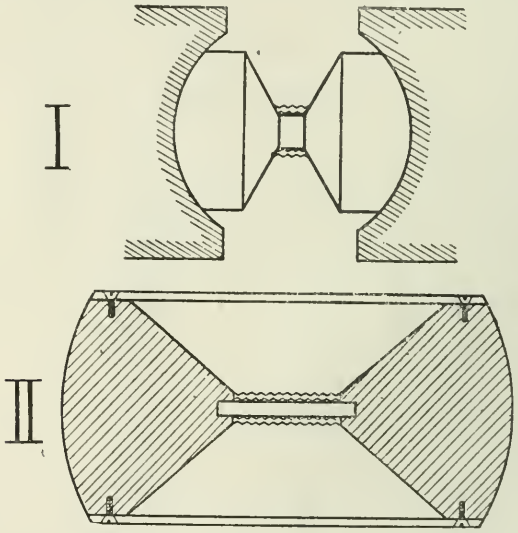


Fig. 1.

turns, when measuring in weak fields the sensibility of the ballistic galvanometers is not sufficient ; on that account the isthmus measurements in strong fields cannot be made to follow directly on the yoke measurements in weak fields, although it is desirable that the measurements should be continuous. These difficulties were overcome by applying always the same cone of soft iron, and by making only the isthmus piece out of the material to be examined. The latter was made 3 mm. thick and 28 mm. long, and was inserted on both sides 4 mm. into the ends of the hollowed-out cone. The two coils, occupying the whole free space of 20 mm., were each wound in two layers on a separate tube which slipped over the isthmus, and they were cemented together ; they can therefore also always be exchanged. In consequence of the large number of the turns their area can very well be determined by means of a magnetic field of known strength ; lastly, for the same reason, the measurements can be begun in weak fields of 100 or 150 gauss, so that direct continuation with the yoke measurements is secured. The apparatus described allows us to attain with the small model of the

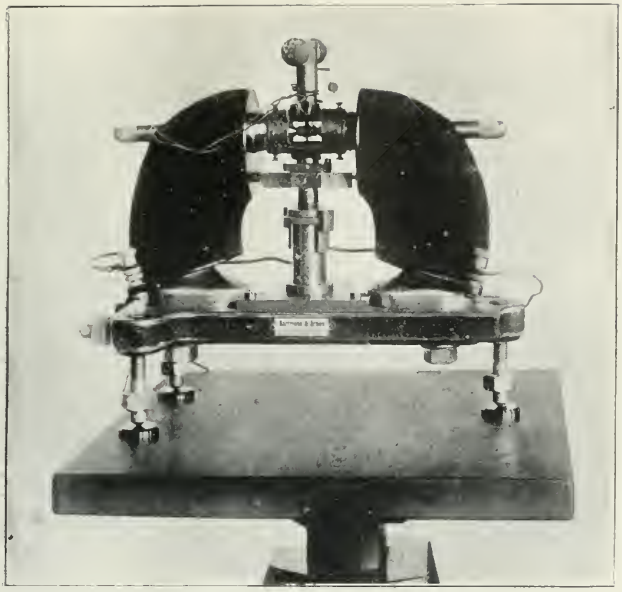


FIG. 2.

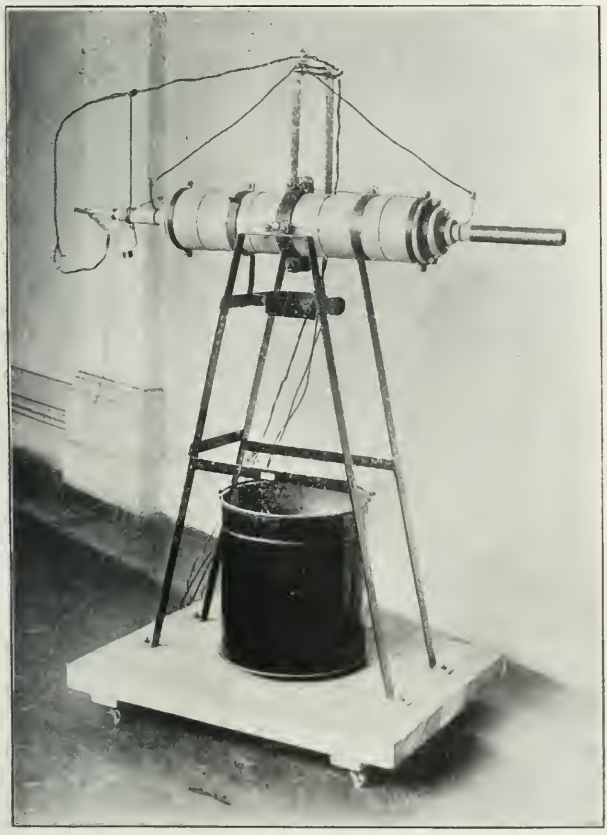


FIG. 3.

du Bois electromagnet a field of about 6,500 gauss, which is mostly quite sufficient for the measurement of the saturation; only in some extremely hard steels the limit of the saturation has not yet been reached. Fig. 2 is a diagram of the whole apparatus.

Besides the magnetic properties, the electric resistance w of the samples was also measured by sending an electrical current i through the rod and determining the potential difference iw between two edges placed on the rod by the compensation method.

As regards the treatment of the samples, one series of the rods was heated for a short time in a vacuum to 930° and slowly cooled, so that the carbon present would be surely secreted in the form of pearlite or of cementite. Other series were heated to 750°, 800°, 850°, 900°, 950°, 1,000°, and 1,100°, and

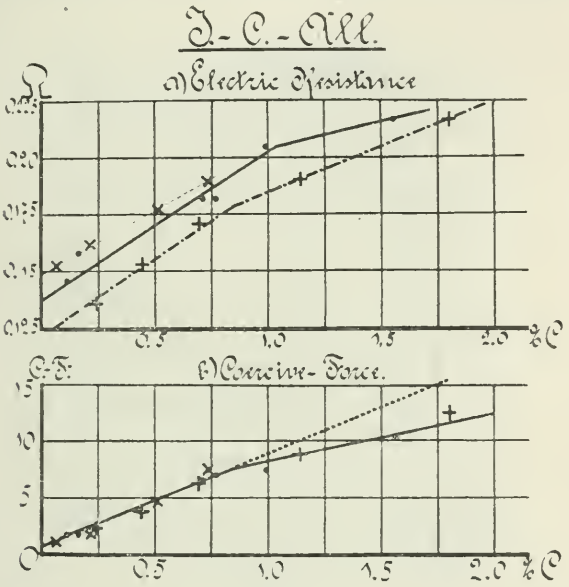


FIG. 4.

hardened in ice-water. Not to be obliged to make a whole new series of rods for every hardening temperature, however, some series were hardened successively at different temperatures. That process is indeed not quite free from objections, because it is not certain that the content of carbon is not diminished a little by the repeated processes of hardening. In that manner, for example, the fact would be explained that by hardening a rod three times at the same temperature the coercive force sank continually from 18·8 to 14·1 gauss.

For hardening the rods an electrically heated furnace was used, a view of which is given in Fig. 3. It is composed of several concentric tubes, on one of which is wound the heating bobbin of platinum foil, while the outer tubes provide for a good distribution of the heat. The rod in the middle of the furnace, the temperature of which is measured by a thermocouple, falls, when the furnace is tilted about its horizontal axis, in a fraction of a second into a vessel filled with ice-water, where it is immediately caught by a stirring apparatus and is quickly cooled.

The Results of the Measurements of Ferro-Carbon Alloys.

The electric resistance of the slowly cooled alloys rises per 1 per cent. C by about 0·06 ohm per m. and sq. mm. The upper part of Fig. 4 illustrates the results; the abscissæ are the percentages of carbon, and the ordinates the resistances per m. and sq. mm. It is obvious that the percentage of Mn and Si strongly affects the absolute value of the resistance; for the series (×) with the largest percentage of Mn stands highest, the series (+) with the smallest impurities lowest. But taking the specimens of each series together, it is evident that both series with higher percentage of C show a bend at about 1 per cent. C. Since the carbon when present to about 1 per cent. exists in the form of pearlite, and at higher contents in the form of cementite, this bend seems to indicate that the same percentage of C in the form of cementite diminishes the electric conductivity less than in the form of

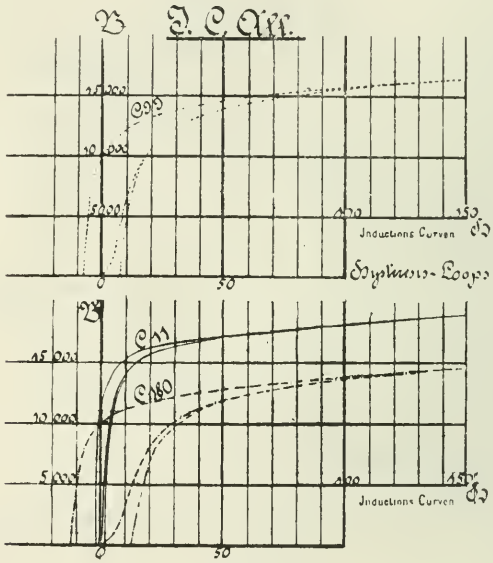


Fig. 5.

pearlite, although one constituent of the pearlite is also known to be cementite. That fact would be entirely explained by the lamellary structure of the pearlite.

On the other hand there seems to be a certain difference between the effect of under-eutectic and over-eutectic cementite. This assumption is supported by the fact that the coercive force shows the same phenomenon as the resistance, whilst it is not probable that the lamellary structure of the cementite in the pearlite would also influence the coercive force. In the lower part of Fig. 4, which represents the relation between the coercive force and the percentage of carbon, the experimental values for alloys up to about 1 per cent. C are lying on a straight line, but the points corresponding to the higher alloys are considerably lower. Thus here again we find a bend near the eutectic alloy, and it must be assumed that over-eutectic cementite causes a relatively smaller increase in the coercive force, and therefore in the magnetic hardening of the iron, than under-eutectic cementite.

The hysteresis loops of the alloys after annealing present the typical appearance; with an increasing percentage of carbon they always become broader and lower; thus the maximum permeability sinks from about 3,300 at 0·06 per cent. C to 450 at 1·8 per cent. C. Examples are shown in Figs. 5 and 6, illustrating the hysteresis loops and the permeability curves of the alloys with 0·11 per cent., 1 per cent., 1·8 per cent. C.

The saturation values in their dependence upon the percentage of C are represented by the upper part of Fig. 7. Disregarding the uncertainty caused by the foreign substances for which we cannot yet allow, we find nearly a straight line. The value of the saturation $4\pi I_{max.}$ diminishes by about 1,400 per 1 per cent. C; therefore, if the value of the saturation of the pure iron is assumed to be $4\pi I_{max.} = 21{,}600$, that of the pearlite would be about 20,200, and that of the cementite can be calculated to be about 12,500.

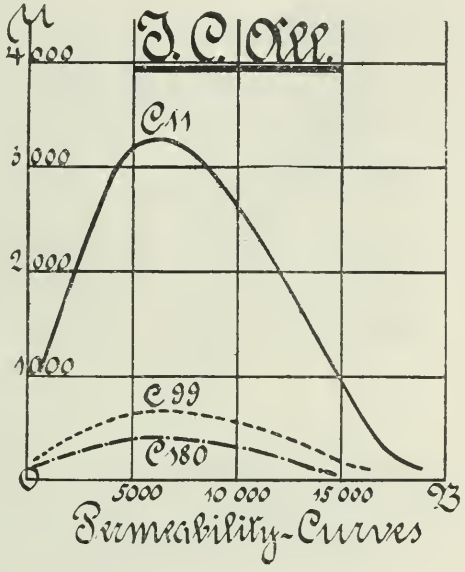


FIG. 6.

An attempt will shortly be made to obtain by direct measurements not only the values of saturation, but also the hysteresis loops of cementite.

In the lower part of Fig. 7 the saturation values of carbon alloys after hardening at 850° are indicated by the small circles. The production of good specimens is not easy, because the hardening process must be very uniformly carried out, and the conditions are very inconstant. However, it is obvious that the points observed are situated nearly on a straight line, that consequently the value of the saturation of iron diminishes approximately in proportion to the percentage of dissolved carbon, viz., by about 3,000 per 1 per cent. C; this can, of course, be explained only by the fact that the specific gravity of the dissolved cementite cannot much differ from that of the pure iron. The last two points, for 1·57 per cent. C and 1·8 per cent. C, are situated somewhat higher, the cause of which is evidently that at 850° the contents of carbon have not entirely been dissolved yet, but a small quantity of carbon has remained in the form of cementite. The lower portion of the

curve should have the same inclination, therefore, as the upper curve for the annealed alloy.

Corresponding measurements after hardening at 1,100° have not yet given any satisfactory result.

In Fig. 8 the hysteresis loops of the same carbon alloys, examined previously after the annealing process, are shown after quenching at 850°. It is obvious how much, with increasing percentage of C, the induction diminishes in a field of 300, while the coercive force grows.

The dependence of the coercive force upon the percentage of carbon was determined for all the quenching temperatures applied. Fig. 9 gives some examples for the temperatures 800°, 900°, 1,100°. Very interesting is the sharp bend at about 1 per cent. C. Up to this point the coercive force rises in a straight line by about 64 gauss per 1 per cent. C ; beyond that point it

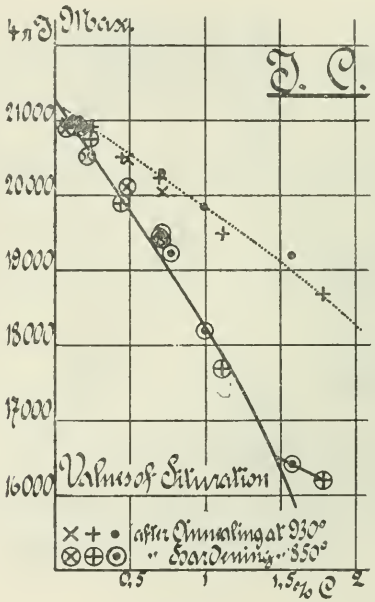


Fig. 7.

becomes nearly constant and almost independent of the contents of carbon. Thus we may say that for a hardening temperature of 800° and also 850° the coercive force rises directly in proportion to the percentage of *dissolved* carbon. If this conclusion be right, then the coercive force of the higher carbon alloys should also increase with rising hardening temperature, because the dissolving power of the iron for carbon grows with the increase of temperature. That is indeed the case, for in the alloy with 1·8 per cent. C the coercive force rises from 56 gauss at 750° hardening temperature to the value of 70 gauss at 950° hardening temperature, which is enormously high for a pure carbon alloy ; but then it sinks again to 48 gauss after hardening at 1,100°. This diminution, however, appears, as the figures show, only in the higher alloys and especially in electro-steel ; in the lower alloys, up to about 0·4 per cent. C, it is scarcely to be noticed. In this manner, the curve, which at a hardening temperature of 800° was composed of two straight lines, bends more and more downward. The photomicrographs of these

specimens, taken by Professor Goerens, show that this phenomenon may chiefly be traced back to the formation of austenite at high hardening temperatures and to high percentages of carbon.

In the same manner the electric resistance, like the coercive force,

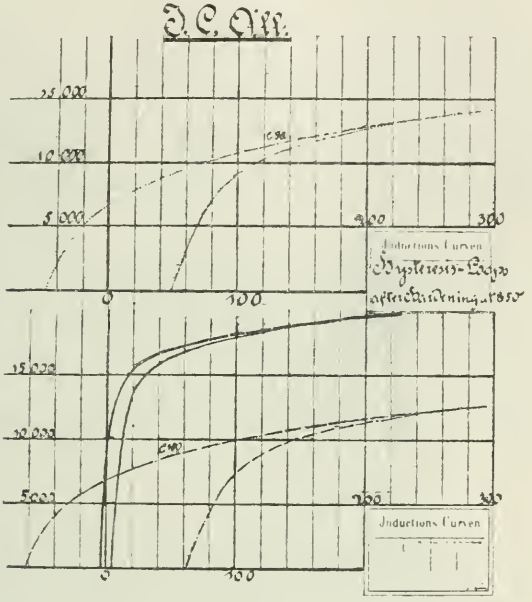


Fig. 8.

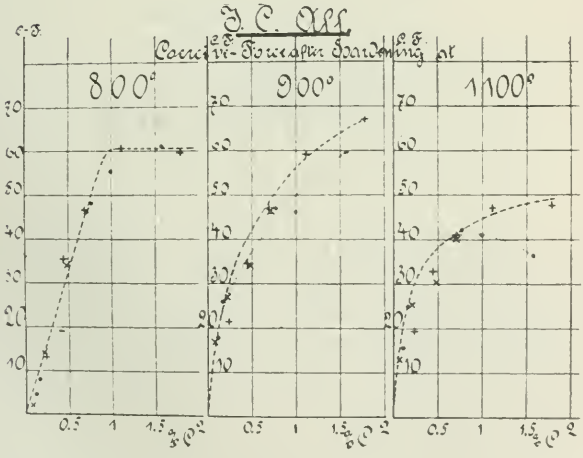


Fig. 9.

depends on the carbon *dissolved* in the iron. Fig. 10 gives the diagram for the electric resistance per m. and sq. mm. as dependent on the contents of carbon for the hardening temperature of 850°. The increase of the resistance with the growing percentage of carbon is much greater than in the case of

annealed alloys ; that is to say, 0·35 ohm per 1 per cent. C, and is expressed by a nearly straight line. A sharp bend takes place at the same point, as in the diagram for the coercive force, and in the same manner the resistance of the highest alloys rises at higher hardening temperatures, at which more carbon is found in a state of dissolution.

Very interesting is the connection between the remanence and the contents of carbon and the hardening temperature. By remanence in this case is to be understood the *true* remanence which we observe when we examine a closed ring or a rod in the yoke ; for this remanence alone is characteristic of the material. The *apparent* remanence, on the contrary, which we observe in a magnet of the shape of a rod or a horseshoe, is much influenced by the coercive force and by the shape of the specimen, and can therefore have very different values for the same material.

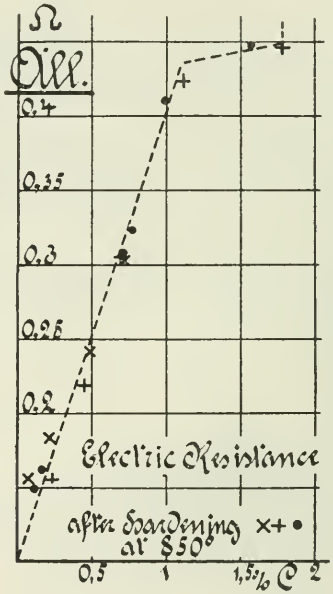


Fig. 10.

It has not so far been possible to establish a general rule for the true remanence ; we only know that the remanence can reach very high values (as high as 15,000) with pure, soft iron, while harder materials, such as steel, alloys, &c., generally have a smaller remanence. Nor has any relation between the carbon percentage and the remanence been observed in the annealed carbon alloys, the carbon of which exists in the form of cementite. But I have found it in the hardened alloys. In Fig. 11 this relation is illustrated for the hardening temperatures 800°, 900°, 1,100°, as was done before with the coercive force.

It will at once be seen that the alloys produced by the different iron-works, which also vary in their contents of Mn and Si, give separate curves ; the values of the higher alloys of electro-steel (.) especially are much lower throughout than those of the chemically purer specimens (+) ; the cause of this has not yet been found. Without counting the lowest alloys up to C 44, which appear to be in an unstable condition, it results that the remanence

diminishes nearly in proportion to the percentage of the *dissolved* carbon. The parts of the diagram between 0·44 per cent. C and 1·14 per cent. C which refer to all hardening temperatures between 850° and 1,100°, and not only those here recorded, agree indeed so closely that the conclusion seems to

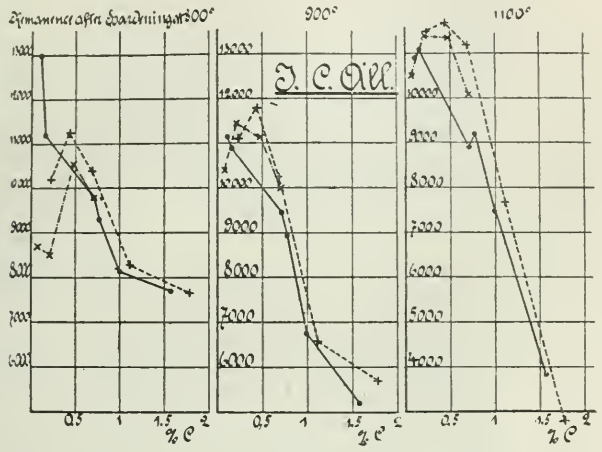


FIG. 11.

be justified that within this range there corresponds to certain contents of carbon also a certain remanence; the hardening temperature is here of no consequence. In the higher alloys, with 1·56 per cent. and 1·8 per cent. C, the more carbon will, of course, be dissolved in the iron the higher the hardening

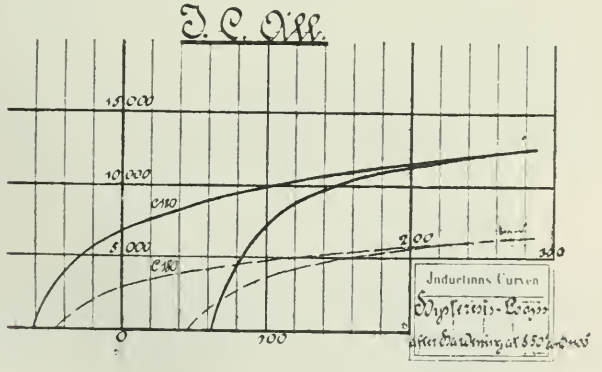


FIG. 12.

temperature, and indeed both alloys finally, at a hardening temperature of 1,100°, come down to the exceedingly low values of 3,800 and 2,800.

Here also all the hysteresis loops become extremely low, as Fig. 12 shows; it represents the hysteresis loop after hardening at 850° and 1,100° for the alloy containing 1·8 per cent. C. That again seems to be an effect of the austenite, the magnetic properties of which are still unknown or uncertain.

If now, as has just been shown, with an increasing percentage of dissolved carbon the coercive force increases, whilst the remanence decreases, there is no possibility, at least for pure carbon alloys, of joining high remanence and high coercive force, as we desire to do in permanent magnets. An attempt must hence be made at least to unite the relatively most advantageous conditions; that is to say, as a rule the hardening temperature should neither be taken below 800° nor above 950°, and the percentage of carbon should be adapted to the shape of the magnet. If the permanent magnet to be produced is to receive the form of a straight rod or of a nearly closed ring or of a horseshoe with a very narrow gap, the best results would be given by relatively low carbon contents, about 0·5 per cent.; for in that case the most important matter is a high *real* remanence, whilst the demagnetising effect of the ends will be rather small and in consequence the amount of coercive force not very essential. If, on the contrary, it is a question of a short, stout rod or a horseshoe magnet with a broad pole-gap, &c., a high percentage of carbon is to be preferred, which will indeed give a small real remanence only, but a large coercive force, so that the demagnetising effect of the ends will be relatively small.

Whether and in how far the addition of other elements often used in the manufacturing of permanent magnets, such as tungsten, molybdenum, chromium, &c., will influence these rules, must be reserved for a later investigation.

The photomicrographs reproduced here (Figs. 13 to 19) generally confirm the deductions from the physical researches. We see first some carbon alloys after hardening at 750° (Fig. 13): alloy with 0·11 per cent. C; the light (clear) part is ferrite, the dark martensite, as will be recognised in more highly magnified reproductions. With an increasing percentage of carbon, the area of the martensite also increases, as is seen from Fig. 14 (C 23) with 0·23 per cent. C, and Fig. 15 with 0·51 per cent. C. In Fig. 16 (C 114) with 1·14 per cent. C the martensite appears already surrounded by cementite, and more so still in Fig. 17 (C 156) with 1·56 per cent. C. Here the martensite has a very delicate structure. The coercive force of that material was comparatively high, viz., 58 gauss. After hardening at 1,000° this material shows a much coarser structure (Fig. 18); the coercive force had decreased to 43 gauss. Finally, after hardening at 1,100° (Fig. 19), the coercive force is not more than 36 gauss; the structure presents the typical appearance of a steel with a certain quantity of austenite, which seems to be the reason of the much worse magnetic properties.

Ferro-silicon Alloys.

When in 1900 Messrs. Barrett, Brown, and Hadfield published the results of their interesting researches on the magnetic properties and the electric resistance of iron-aluminium alloys and iron-silicon alloys, I had the idea to utilise the high specific resistance of the silicon alloys for the diminution of the eddy currents in transformer and dynamo sheet metal. The P.T.R. therefore requested some prominent German firms to produce transformer sheets out of silicon alloys, and began itself to make experiments with the new material. It resulted in the course of these experiments that more had been attained than had been expected; for not only were the eddy currents weakened in accordance with the higher specific resistance, but also the hysteresis loss was often smaller, and the permeability in low fields was higher than in the usual dynamo iron. Thus the so-called "legierte Blech" could not fail almost entirely to replace the usual material within

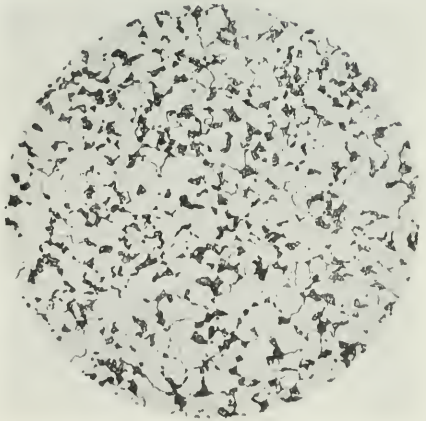


Fig. 13.

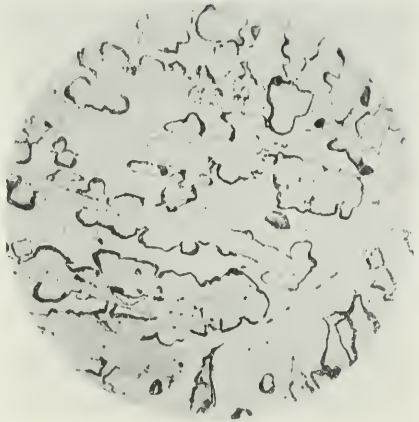


Fig. 14.

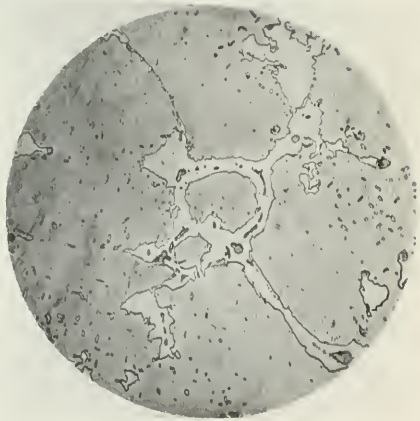


Fig. 15.

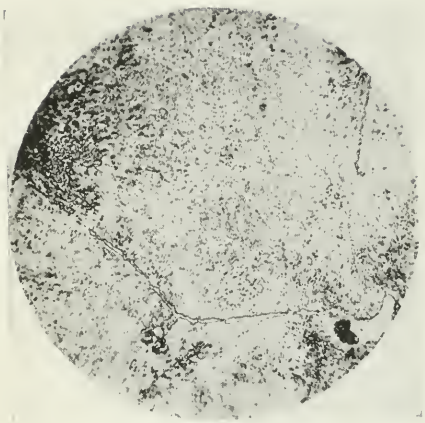


FIG. 16.

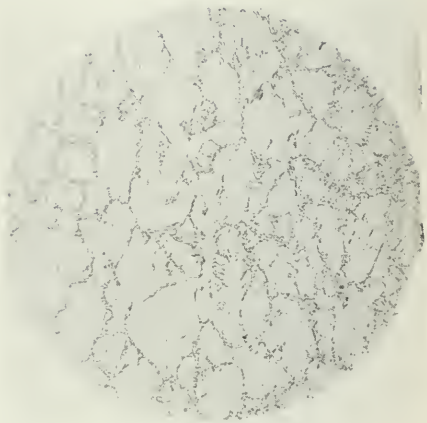


FIG. 17.

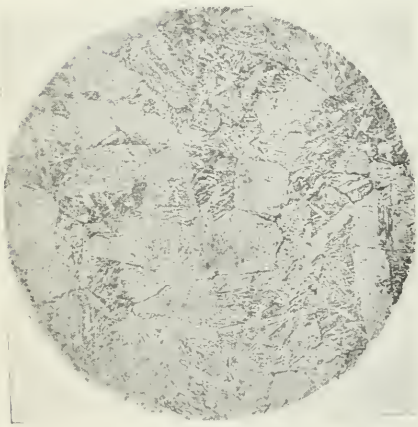


FIG. 18.

FIG. 19.

a short time, in spite of the initial difficulty of production and of the much larger price, and German electrical engineers are much indebted to Messrs. Barrett, Brown, and Hadfield for the researches which supplied the foundation for this great improvement in transformer material.

The question in which way the addition of silicon may improve the magnetic properties of iron still awaits explanation. Let me outline the opinion to which the experiments conducted in the P.T.R. have led me.

I do not believe, in the first instance, that the silicon has a *directly* improving influence on the iron. If it were so, the magnetic properties of the alloys must improve in *proportion* to the increasing contents of silicon; that is, the coercive force must decrease, the maximum permeability and the value of saturation must rise; but that is not so. In the following figures examples are given of the results of the measurements made in the P.T.R.

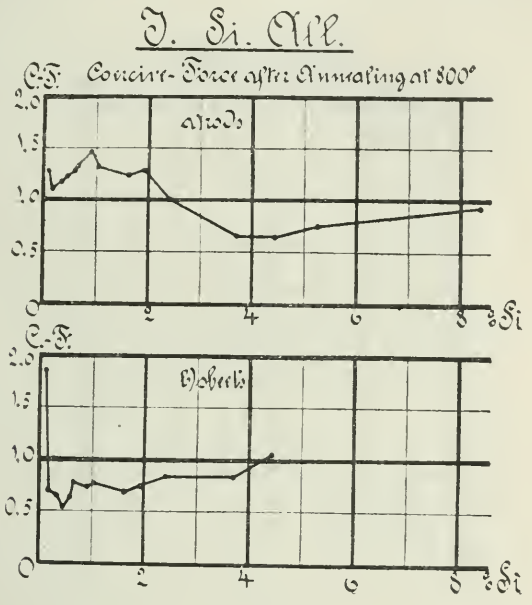


FIG. 20.

Fig. 20 gives the dependence of the coercive force upon the percentage of silicon after annealing at 800°, the upper part referring to rods containing up to 8·6 per cent. of silicon, the lower part sheets with up to 4·5 per cent. Quite analogous are the results (not here reproduced) obtained after annealing at nearly 1,000°. The observed values of the coercive force are joined by straight lines. The material of the rods and sheets is the same; it was kindly supplied to the P.T.R. by the firm of Krupp at Essen and rolled out by the firm of Capito and Klein at Benrath.

The first point concerns the coercive force of the original material containing about 0·06 per cent. Si only; the coercive force is in both cases rather large. In the rods as well as in the sheets a very great improvement is occasioned by the addition of about 0·1 per cent. Si. This increase continues in the sheets; the lowest value of 0·54 gauss is reached already with 0·4 per cent. Si; by higher percentages the material is again deteriorated.

The material of the rods from 0·15 per cent. Si upwards does not improve

at first with a rising Si percentage, but deteriorates; with 1 per cent. an improvement sets in which continues up to about 4·5 per cent. Si; with a larger percentage of silicon the coercive force rises again. Higher annealing temperatures are rather more advantageous for high-grade alloys, but the difference is of no consequence.

The diagrams show rather clearly that the dependence of the coercive force upon the percentage of silicon is very irregular.

This is seen still more distinctly in the maximum permeability $\mu_{max.}$, the variation of which is represented for rods and sheets in Fig. 21, after annealing at 800°. In the rods the difference is not very great; the values certainly are relatively high for a high percentage of silicon, but just in the richest alloy the maximum permeability decreases again. The examination of the sheets leads to very irregular results. Here the highest value of the maximum

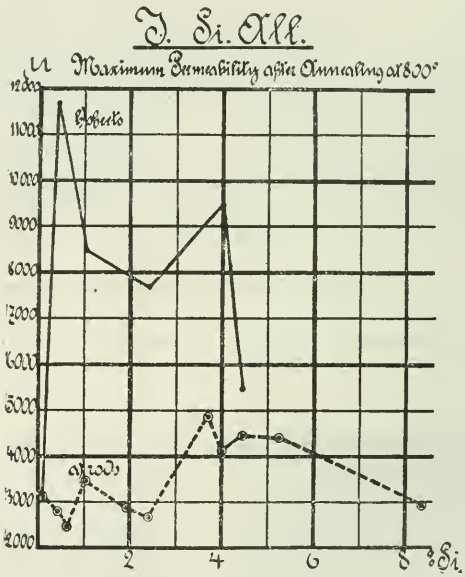


Fig. 21.

permeability occurs in the alloy with only 0·4 per cent. Si; with an increasing percentage the values even decrease considerably.

But the saturation values, $4\pi I_{max.}$, the variations of which are shown in diagram (Fig. 22), bear the strongest evidence against the supposition that silicon has a directly improving influence. These saturation values do not increase with the growth of the percentage of silicon, but they decrease, and the change takes place along a curve, the upper portion of which, up to about 4·5 per cent. Si, may approximately be considered as a straight line; the decrease amounts to about 500 maxwells per 1 per cent. Si. It may therefore be said: The silicon is acting like a foreign substance, which diminishes the active cross-section of the iron, and diminishes in consequence the value of the saturation. Messrs. Hopkinson and Hadfield came to the same result in the account of their researches published last year, "The Magnetic Properties of Iron and its Alloys in Intense Fields." *

* *Journal of the Institution of Electrical Engineers*, 46, 235–309, 1911.

It may then be taken for granted that the effect of silicon is not a direct, but an indirect one, and the question arises, of what kind is this indirect effect? Here also Messrs. Hopkinson and Hadfield have already suggested an explanation, saying that the silicon seems to neutralise to a certain degree the effect of the carbon on the value of saturation. I arrived at the same conclusion some years ago already on the strength of numerous measurements. Indeed, I believe that this influence is much more effective still in the region of the low inductions than in that of the high ones, which Messrs. Hopkinson and Hadfield had especially in view, and that the value of the coercive force in particular and therefore of the hysteresis loss, which is approximately in proportion to the coercive force, is very much influenced by the silicon. I would like to go a little further into this question.

I mentioned before that the increase of the coercive force by 1 per cent. C is about 7·5 gauss if the carbon exists in the form of cementite but at least

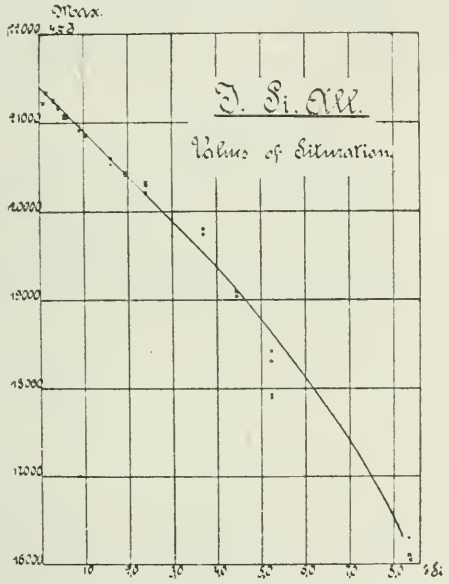


FIG. 22.

60 gauss if it is dissolved in the iron. Now there were among the silicon alloys examined in the form of rods several with relatively high contents of carbon, as may be seen from Table II.

If these amounts of carbon had been dissolved in the material, they should have produced approximately the values of the coercive force marked in the fourth column; but if in the form of cementite, the values in the fifth column, assuming that the original material (without carbon) had a coercive force of 0·7 gauss. In reality, there were found for the coercive force, before annealing at 700°, the values of column 6; after annealing at 700°, the values of column 7; after annealing at 975°, the values of column 8. And here it must be mentioned that the two first numbers, 30 and 50, were cast in the shape of stout blocks afterwards cut up; the two last, 52 and 85, on the contrary, in the form of thin rods about 1 cm. in diameter; the latter have therefore cooled rapidly, the former slowly. That is the reason why the coercive force of the two latter has been relatively high before annealing,

especially that of number 85. Evidently a small quantity of C has remained in a state of dissolution. In the three other alloys, however, the coercive force is already less before annealing than it should be according to the contents of carbon, if this had existed in the material in the form of cementite; therefore part of the carbon must have been secreted already during the cooling process after the casting in the form of the passive temper-carbon (graphite). After annealing at 975° for twenty-four hours, the carbon seems entirely to be secreted in the form of temper-carbon, for the coercive force is, as column 8 shows, as small as that of pure iron, which scarcely contains any carbon. In the higher alloys, Nos. 50 and 52, this segregation occurs already after annealing at 700°, for the coercive force has, as column 7 shows, already gone down to very low values.

On the other hand, the coercive force of the *low*-grade Si alloys in the form of rods is still very high, about 1·2 to 1·5 gauss, and is only slightly influenced also by the height of the annealing temperature, whilst it decreases in the same alloys to about half its value, if these are rolled to sheets. The enquiry into the explanation of the fact that the magnetic properties of low-grade alloys in the shape of sheets are generally much better than those of rods, is not yet finished.

TABLE II.

1	2	3	4	5	6	7	8
			Coercive Force.				
Specimen Number.	Percentage of		C dissolved.	C in form of Cementite.	Before Annealing.	After Annealing	
	C	Si.				At 700°.	At 975°.
30	0·21	2·4	13	2·3	1·30	1·19	0·70
50	0·29	4·5	18	2·9	1·26	0·65	0·69
52	0·18	5·25	11	2·1	1·93	0·70	0·59
85	0·34	8·35	20	3·2	6·56	4·60	0·70

From the same point of view the facts can be explained which are observed in hardening silicon alloys with a considerable percentage of carbon. Even when the material had not been annealed before, the coercive force after quenching is not nearly so high as in the pure carbon steel of the same carbon percentage. For instance, an alloy with 4·4 per cent. Si and 0·29 per cent. C, after quenching at 950°, yielded a coercive force of 6 gauss, whilst a pure carbon steel of the same percentage of carbon under identical circumstances would have shown a coercive force of about 33 gauss. The effect becomes still more surprising when the material had previously been *annealed* for a longer time. The same material, after having been annealed for twenty-four hours at 800°, showed when hardened at 850° only a coercive force of 0·76 gauss, so that surely no hardening carbon could have been present in this material. These conclusions were confirmed by the chemical analyses made by the firm of Krupp. In all the specimens examined, which were hardened at different temperatures, the presence of a trace of hardening-carbon could only be proved in one case; in all other cases the considerable amounts of carbon consisted partly of cementite and partly of temper-carbon.

An observation made during the study of the transition-points of the iron-silicon series will finally have a certain interest in this respect. The first

transition-point was observed by the Roberts-Austen method, the second by the deflection of the magnetometer. The latter can be observed under all circumstances with sufficient exactitude, whilst the former is only then clearly to be seen when the material forms pearlite. These transition-points are shown on the diagram, Fig. 23, where the abscissæ give the percentages of silicon in the alloys and the ordinates the temperatures of the first and second transition-points. It appears striking at first that the second magnetical transition-point is lowered by an increasing percentage of silicon, whilst the first, pearlitic transition-point, the mean between Ac_1 and Ar_1, rises even above the second. The two coincide for 2·2 per cent. Si. Up to 2·4 per cent. Si, the first pearlitic point of transition can also be well perceived, but in the higher alloys it cannot be traced at all, though the absolute percentage of carbon rises also with the increasing contents of silicon, and grows, as has already been mentioned, to about 0·3 per cent. This fact can scarcely be explained in any other way than by assuming that in these high-grade silicon alloys the possibly present pearlite is transformed into temper-carbon already during the slow heating up to about 800°.

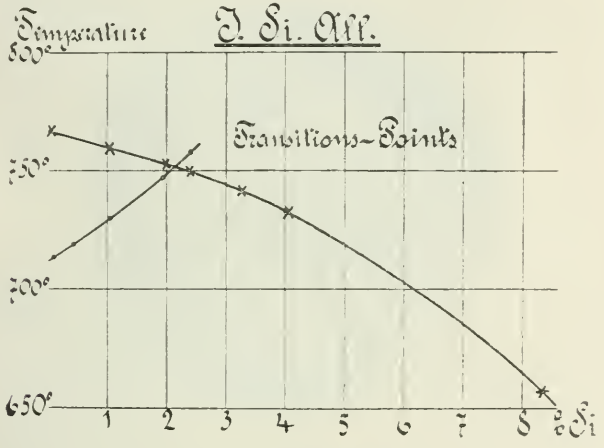


Fig. 23.

It was to be hoped that these conclusions as to the influence of Si on C would be supported by the micrographic study, and this is indeed the case, as the following examples (Figs. 24 to 30) will demonstrate. The first are photographs of untreated iron-silicon alloys enlarged a hundredfold (Fig. 24), Si 10 ; 1 per cent. Si ; 0·2 per cent. C (Fig. 25), Si 30 ; 2·4 per cent. Si, 0·2 per cent. C (Fig. 26), Si 50 ; 4·5 per cent. Si ; 0·29 per cent. C. The structure of all these alloys is clearly pearlitic, as will immediately be recognised by examining the last specimen with an enlargement of 750 diameters (Fig. 27). This pearlitic structure has been preserved almost unchanged after annealing at 700° for twenty-four hours in the low alloys and up to 2·4 per cent. Si (Fig. 28), that is, up to the highest alloy in which the pearlitic transition-point could still be distinguished, but no longer in Si 50 with 4·5 per cent. Si and 0·29 per cent. C (Fig. 29). Here the pearlite has entirely disappeared, and in its stead enclosures of temper-carbon have appeared ; but at the same time the coercive force has decreased from 1·26 to 0·65 gauss.

But the reverse takes place, even after annealing at 975°, in the original

material, which contains only very little silicon (0·06 per cent.) ; the content of pearlite has entirely remained unchanged (Fig. 30) ; as the percentage of carbon is not small (0·15 per cent.), the rather high coercive force of 1·5 gauss observed in this material even after annealing needs no further explanation.

These results seem to justify the following conclusion. The presence of larger amounts of silicon prevents, even with rather quick cooling, the formation of the extremely injurious solid solution of carbon and iron ; the contaminations with carbon appear only in the shape of the much less injurious pearlite. Even the pearlite is decomposed by a prolonged process of annealing, under the influence of the silicon, into ferrite and temper-carbon, and thus becomes magnetically almost quite passive. To produce this effect with certainty, however, there must be at least from 3 to 4 per cent. of silicon in the material. The fact that thin sheet-metal containing smaller amounts of silicon may show exceedingly good magnetic properties must have other reasons.

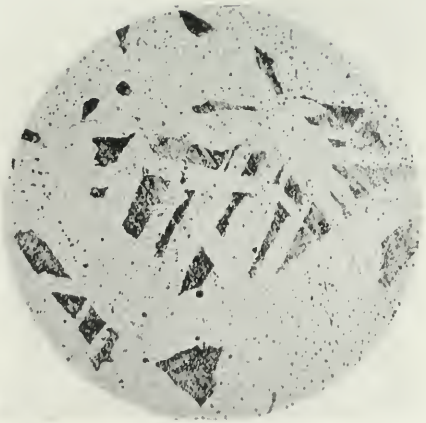


Fig. 24.

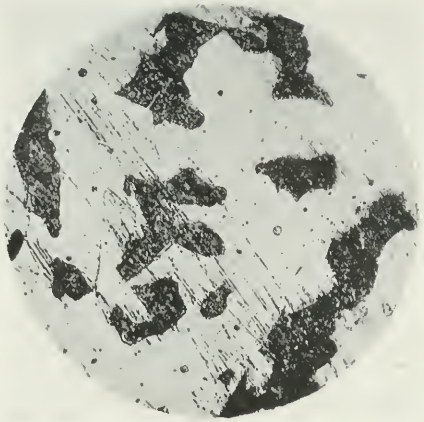


Fig. 25.

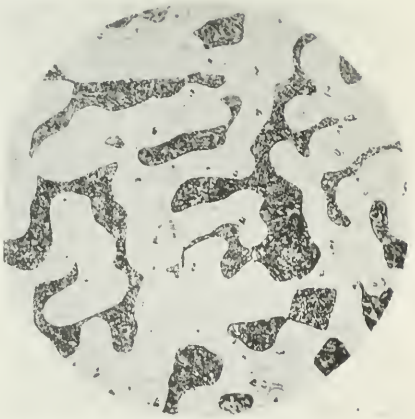


Fig. 26.

FIG. 27.

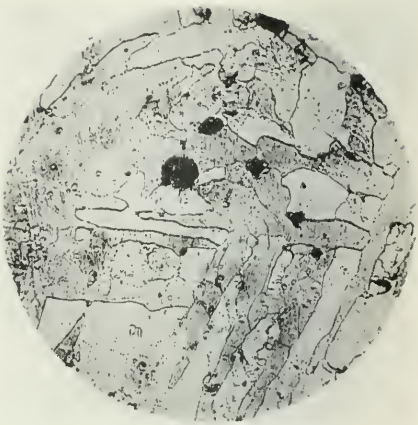


FIG. 28.

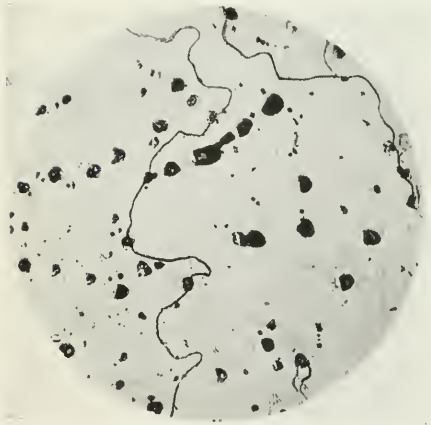


FIG. 29.

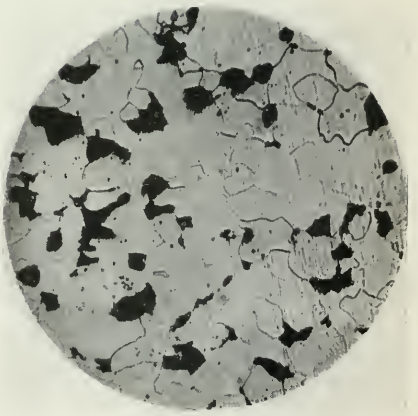


FIG. 30.

ON THE MAGNETIC PROPERTIES OF A VARIETY OF SPECIAL STEELS AT LOW TEMPERATURES.

Dr. James G. Gray, D.Sc., F.R.S.E. (Lecturer on Physics in the University of Glasgow) and **Dr. Alexander D. Ross, M.A., D.Sc., F.R.S.E.** (Lecturer on Natural Philosophy in the University of Glasgow) contributed a Paper "On the Magnetic Properties of a Variety of Special Steels at Low Temperatures," which was read by Dr. Ross.

The first experimenter to show that temperature has a marked influence upon the magnetic properties of iron was Gilbert, who at the end of the sixteenth century discovered that an iron needle, when raised to a red heat loses its power of being attracted by a lodestone, and that it recovers its magnetic property on cooling. Quantitative measurements on the variation of magnetism with temperature were first made by Coulomb. During the period extending from 1870 to 1890 a great amount of work was carried out in this field of research, notably by Rowland,* Baur,† Trowbridge,‡ Perkins,§ Tomlinson,‖ and Hopkinson,¶ who investigated the changes in the magnetic properties brought about by temperature in iron, nickel, cobalt and carbon steels.

It is now well known that the effect of raising the temperature of a test-piece of iron or steel is to bring about an increase in the permeability for low values of the magnetising force, and to diminish the permeability for high fields. Thus if the magnetisation curves yielded by a specimen at temperatures t_1 and t_2 ($t_2 > t_1$) are plotted, that corresponding to t_2 will lie initially above, and finally, below that corresponding to t_1. To account for this result, Hopkinson regarded the iron or steel as made up of permanently magnetic molecules, the axes of which become more or less directed to parallelism by magnetic force. The effect of rise in temperature is to diminish the magnetic moment of the molecules, gradually at first, but more and more rapidly as the critical temperature is approached. On the other hand, the freedom with which the molecules allow their axes to be directed increases with rise of temperature ; in the case of low fields the increased freedom of the molecules brought about by increase in the temperature more than compensates for the diminution in the magnetic moment of the molecular magnets, with the result that the permeability of the test-piece is increased. For high values of the magnetising force the reverse is the case.

Fleming and Dewar** in 1896 studied the effect produced upon the magnetic properties of Swedish iron by cooling it to the temperature of liquid air. In annealed specimens they found the permeability for all fields less at

* *Phil. Mag.*, xlvii., p. 321, 1874.
† *Wied. Ann.*, xi., p. 394, 1880.
‡ *Proc. Amer. Acad.*, p. 462, 1885.
§ *Sill. Journ.*, xxx., p. 218, 1885.
‖ *Phil. Mag.*, xxv., p. 372, 1888.
¶ *Proc. Roy. Soc.*, xlv., p. 318, 1889.
** *Proc. Roy. Soc.*, lx., pp. 57 and 81, 1896.

— 190° C. than at room temperature, while for unannealed or case-hardened iron they found the permeability enhanced at low temperatures, the improvement in magnetic quality being the more marked the harder the iron.

It is to be observed that we should infer from Hopkinson's work that the effect of cooling a specimen in liquid air would be to diminish the permeability for low fields and to increase it for high fields. The work of Dewar and Fleming was confined to low fields, and no crossing of the magnetisation curves of the specimens corresponding to room temperature and — 190° C. was observed.

More recently Honda and Shimizu* have examined a number of materials at the liquid air temperature. They find that the effect of the low temperature is to diminish the permeability for low fields and to increase it for high fields, which is what is to be expected. The abnormal behaviour of steel observed by Dewar and Fleming was not confirmed.

The experiments described in the present paper were carried out on specimens in the form of cylindrical rods. The steels were all prepared by Messrs. Sir W. G. Armstrong, Whitworth and Co. from the same variety of soft iron. The metal was in each case cast vertically in moulds 2·7 in. square, forged to 1·4 in. square, and then rolled into cylindrical rods of about $\frac{3}{8}$ in. diameter. Finally the specimens were turned up into true cylinders, each having a length of 22 cm. and a diameter of 0·9 cm.

The compositions of the specimens are given in Table I. It will be seen that the series embraces a large variety of carbon and other steels.

The conditions in which the steels have been tested are as follows :—

1. Forged and rolled.
2. Normalised.
3. Annealed at 900° C.
4. Quenched at 450° C. in ice-cold water.
5. Quenched at 900° C. in ice-cold water.
6. Re-annealed at 900° C. after quenching at 900° C.

In condition 1 the specimens are in a state of internal strain, brought about by the forging and rolling operations. As a result the material is far from homogeneous, and different specimens of the same steel may exhibit widely differing magnetic properties. The results of the tests carried out with the material in condition 1 are therefore of comparatively little importance and are not included in the tables of results.

The internal strains referred to may be removed by normalising the specimens. This operation consists in heating up the specimen almost to redness and cooling it slowly. The temperature employed is sufficiently high to give the necessary freedom for internal adjustment, and so the metal in condition 2 may be regarded as the normal type of cast material.

Annealing at 900° C. (condition 3) admits of complete structural change in the steel, while the cooling is sufficiently slow to allow the material to assume almost completely its equilibrium condition corresponding to ordinary temperature.

The normalising and annealing operations were conducted as follows. The specimen was embedded in kaolin clay contained in an iron tube which was placed within a Fletcher gas furnace; the specimen could thus be brought to any desired temperature while out of contact with air, and the temperature attained measured by a platinum, platinum-iridium thermo-junction.

Condition 4 was attained by heating the specimen to 450° C. and plunging

* *Phil. Mag.*, x., p. 548, 1905.

TABLE I.

Percentage Composition of the Steels.

Specimen.	Steel.	C.	Mn.	Si.	Cr.	P.	W.	S.
A	Mild Steel	0·30	0·60	0·07	—	—	—	Trace
B	Medium Carbon Steel	0·8	0·20	0·10	—	—	—	,,
C	High Carbon Steel	1·64	0·13	0·12	—	—	—	,,
D	Cast Iron	3·15	0·21	0·75	—	—	—	—
E	Chrome Steel	0·30	0·40	0·25	1·03	—	—	,,
F	Chrome Steel	0·50	0·50	0·29	4·07	—	—	,,
G	Silicon Steel	0·35	0·66	3·47	—	—	—	,,
H	Silicon Steel	0·42	0·71	6·07	—	—	—	,,
I	Phosphor Steel	0·47	0·17	0·27	—	0·168	—	,,
J	Tungsten Steel	0·51	0·13	0·19	—	—	4·01	,,
K	Swedish Soft Iron	0·06	0·10	0·03	—	—	—	,,
L	Sankey Transformer Iron			Composition not determined.				

it into ice-cold water, while condition 5 was arrived at in like manner by heating the specimen to 900° C. and plunging it into ice-cold water. Finally, with a view to ascertaining the effect of the quenching operations upon the material, the specimen was reannealed at 900° C. and re-tested. The results of these last tests showed that the previous heat treatment had not resulted in any disintegration of the metal.

In Fig. 1 is given the equilibrium diagram of the iron-carbon series of steels. Iron in the region below the line *b c e g h* is in the *α*, or magnetic condition, and cannot dissolve carbon. In the region *a c b* it is in the *β*, or non-magnetic condition, and is not a solvent for carbon. In the region *a c e g h* the iron is in the *γ*, or non-magnetic form, in which it readily dissolves carbon up to about 1·8 per cent. A carbon steel ideally quenched

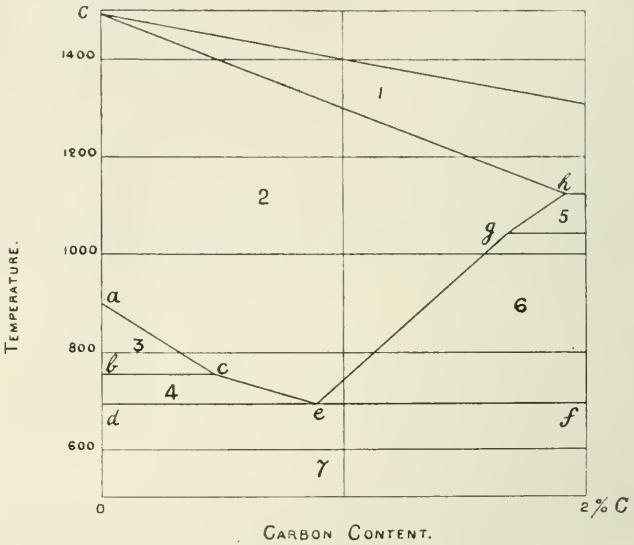


FIG. 1.—Equilibrium Diagram of the Iron-Carbon Alloys.

1 = γ solid solution + liquid.
2 = γ solid solution.
3 = β iron + γ solid solution.
4 = α iron + γ solid solution.
5 = Fe_3C + γ solid solution.
6 = Fe_3C + γ solid solution.
7 = Fe_3C + α iron.

(that is, quenched so suddenly as to fix the constitution obtaining at the temperature of quenching) from a temperature corresponding to a point in the area *a c e g h* should be non-magnetic and should be very hard owing to the hardness of the solid solution of carbon or carbide of iron in γ iron, of which it is composed. An actual quenched specimen is found to be magnetic owing to the partial inversion of the γ into α iron in steels containing more than 0·45 per cent. carbon, and the partial inversions of γ into β and β into α iron in the case of steels with a smaller carbon content. Employment of a temperature as high as 900° C. enables the above-mentioned inversions to be fairly well suppressed, while the use of a higher temperature for quenching would have involved risk of burning the steel and of subsequently cracking the metal on plunging it into ice-cold water.

The quenching at 450° C. (condition 4) is carried out at a temperature below that of the lowest transformation point. The steels in this condition accordingly exhibit the magnetic properties characteristic of the material when hardened only by mechanical means, viz., that due to the sudden cooling and consequent rapid contraction of the outer shell.

It may here be mentioned in passing that the special elements added to form the steels were such as produced no very pronounced change in the character of the equilibrium diagram. The conditions of quenching which have been shown above to be the most satisfactory for the simple carbon steels were thus also those best adapted for the silicon, chrome, phosphor, and tungsten steels.

The tests were carried on a form of magnetometer * designed by the writers. This instrument is provided with facilities for testing specimens at all temperatures lying between that of liquid air and about 1,000° C. Pre-

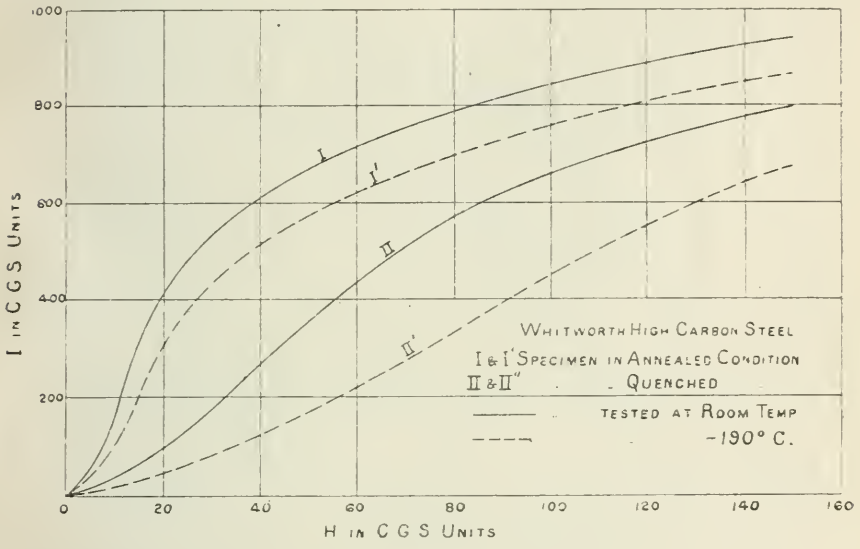


Fig. 2.

liminary experiments were carried out with a view to determining the effective lengths and demagnetising factors of the specimens. The magnetometer is well adapted for the determination of the effective length of a bar. The method employed is the well-known one of testing the specimen in the A and B positions of Gauss, and deducing the distance between the poles.† The demagnetising factors were determined by carrying out a series of tests on a bar 0·9 cm. in diameter and 100 cm. long. The factor for this bar was assumed to be 0·00365. This result is taken from the table of factors prepared by Du Bois,‡ and is in agreement with the work of Riborg-Mann,§ and Ascoli.‖ The bar was then cut up into five test specimens, each

* *Proc. Roy. Soc. Edin.*, xxix., p. 182, 1909 ; *Phil. Mag.*, Ser. 6, xviii., p. 148 (July, 1909).

† A. Gray, *Absolute Measurements in Electricity and Magnetism*, vol. 2, part 1, London, 1893.

‡ *Ann. d. Phys. u. Chem.*, xlvi., p. 485, 1892.

§ *Phys. Rev.*, iii., p. 359, 1896

‖ Rendic, *R. Acad. d. Lincei*, iii., 2. p. 190, 1894, and vi. 2, . 129, 1897.

of length 20 cm., and a series of tests carried out. By comparing the magnetisation curves yielded by the long one with those yielded by the short ones the factors were readily deduced.

It is well known that before commencing a magnetic test the traces of previous magnetic history must be eliminated from the specimen. This is accomplished by subjecting it to the action of an alternating magnetic field, which is very gradually reduced from a large value to zero. The initial value of the alternating field should be greater than the greatest field strength employed in the previous operations. A specimen in the condition brought about by the action of the alternating field is said to be neutral. In what

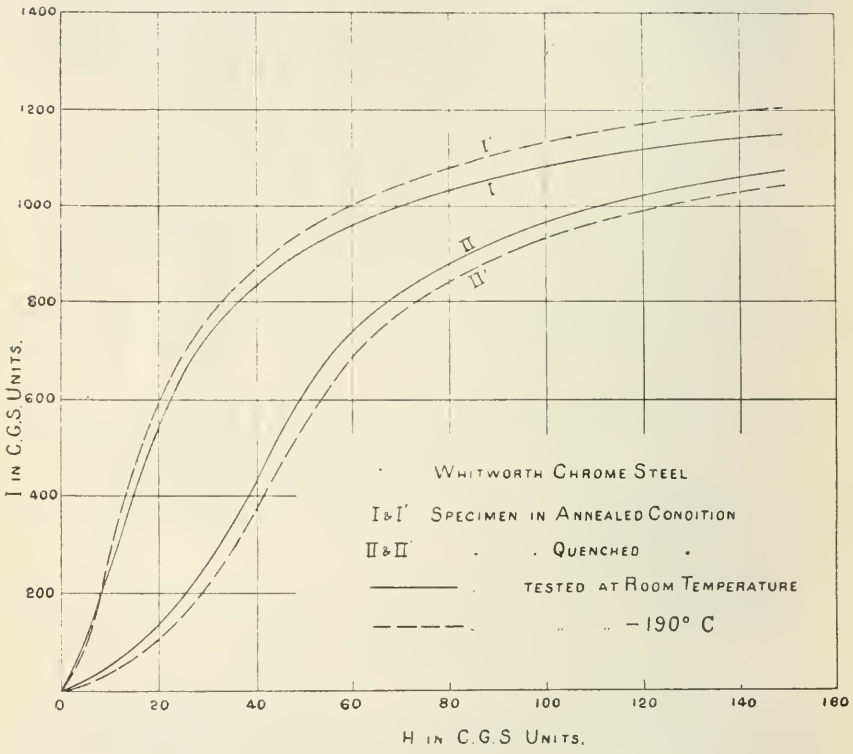


FIG. 3.

follows we shall refer to the process by means of which the specimen is rendered neutral as a "process of reversals."

But it is far from well known that any thermal treatment applied to a specimen between its neutralisation by the process of reversals and the following magnetic tests is fatal to accurate work. A specimen rendered neutral at one temperature ceases to be neutral if the temperature is changed. Before carrying out tests at the new temperature it is essential that the specimen should be subjected to a process of reversals at the new temperature. This important fact has been clearly shown by a number of experiments carried out by the authors.*

The results yielded by the specimens are shown in Tables II. to XI. inclu-

* See *Phil. Mag.*, 6, xxi., p. 1, 1911 ; *Proc. Roy. Soc., Edin.*, xxviii., p. 239 and p. 615, 1908.

TABLE II.

Whitworth Mild Steel, 0·3 C.

Composition.	C, 0·3; Mn, 0·6; Si, 0·07.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	15	10	20	10	14	10	2	1
1	27	20	40	23	30	20	3	2
2	60	42	100	50	75	50	5	3
3	110	70	170	110	160	100	11	8
4	200	120	270	200	350	180	15	11
5	290	200	340	290	460	270	20	16
10	533	510	610	540	680	610	58	46
20	792	770	855	810	870	830	200	140
30	946	926	942	906	960	923	420	312
40	1,036	1,012	1,007	980	1,025	990	622	510
50	1,085	1,042	1,055	1,033	1,075	1,045	755	660
70	1,160	1,045	1,125	1,105	1,150	1,120	903	850
100	1,218	1,210	1,200	1,190	1,220	1,195	1,025	1,005
150	1,270	1,265	1,270	1,260	1,280	1,270	1,125	1,120
Residual magnetism ...	500	510	340	350	350	360	610	620
Coercive force	3·5	4·2	2·5	2·7	3·5	3·0	25	26

TABLE III.

Whitworth Medium Carbon Steel.

Composition.	C, 0·8 ; Mn, 0·20 ; Si, 0·10.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	− 190° C.	15° C.	− 190° C.	15° C.	− 190° C.	15° C.	− 190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	2	1	3	2	1·6	0·8	1	0·6
1	4	3	6	4	4	3	3	2
2	8·6	6·4	14	10	10	8·2	8	6
3	18	14	23	17	18	13	12	9
4	30	20	33	25	28	21	16	12
5	40	29	45	35	40	32	20	14
10	115	80	160	105	135	95	42	30
20	408	280	460	350	450	350	92	72
30	660	500	635	535	630	530	150	120
40	810	650	758	675	745	655	234	188
50	890	750	830	760	830	750	335	264
70	1,000	900	945	880	945	880	550	460
100	1,090	1,040	1,050	996	1,040	1,000	740	660
150	1,180	1,135	1,150	1,115	1,150	1,115	900	850
Residual magnetism ...	560	550	470	430	450	450	490	470
Coercive force	13·2	14·0	11·0	13·0	11·0	14·5	42	48

TABLE IV.

Whitworth High Carbon Steel.

Composition.	C, 1·64 ; Mn, 0·13 ; Si, 0·12.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	6	3	7	3	4	2	2	1
1	11	6	11	5	8	4	3	2
2	18	10	20	10	16	12	8	6
3	28	20	30	20	28	20	12	7
4	40	30	44	30	40	30	16	10
5	52	42	55	35	53	43	20	12
10	170	115	180	110	170	112	42	26
20	410	310	400	325	405	310	100	55
30	540	430	540	435	530	430	170	90
40	620	510	650	530	620	510	270	130
50	690	570	710	590	690	570	360	170
70	750	660	780	670	770	650	510	290
100	845	750	850	760	840	750	660	430
150	940	860	940	870	930	860	800	670
Residual magnetism ...	400	330	370	300	370	300	370	290
Coercive force	10·0	11·0	10·0	11·0	10·0	11·0	32	50

TABLE V.

Whitworth Cast Iron.

Composition.	C, 3·15; Mn, 0·21; Si, 0·75.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	2	1	4	2	3	2	2	1
1	5	3	8	5	6	4	3	2
2	10	8	18	12	15	12	4	2
3	18	16	27	18	25	17	7	4
4	25	22	35	26	33	25	10	8
5	32	29	48	33	42	32	12	10
10	83	68	123	75	105	72	26	22
20	290	180	340	230	320	202	66	52
30	390	290	445	342	440	322	105	92
40	452	365	510	420	510	405	160	136
50	506	420	556	475	560	470	215	185
70	596	506	630	570	640	560	325	292
100	680	590	710	655	710	650	440	440
150	750	700	780	740	760	740	560	580
Residual magnetism ...	315	295	410	370	390	350	345	330
Coercive force	12·5	16·0	14·0	18·0	14·0	18·0	48	51

TABLE VI.

Whitworth Chrome Steel, 1 per cent. Cr.

Composition.	C, 0·30 ; Mn, 0·40 ; Si, 0·25 ; Cr, 1·03.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	8	6	8	6	8	6	2	1
1	14	9	14	10	14	10	5	3
2	30	20	30	22	28	21	7	4
3	50	40	52	41	50	40	10	7
4	70	55	70	54	68	52	14	10
5	96	80	95	82	90	80	20	15
10	300	150	250	270	245	265	50	35
20	630	650	550	590	540	580	125	102
30	830	870	740	770	750	770	260	220
40	930	970	840	870	840	860	440	370
50	980	1,035	900	950	880	930	610	540
70	1,060	1,115	990	1,050	960	1,020	730	680
100	1,130	1,190	1,070	1,140	1,040	1,110	820	780
150	1,220	1,270	1,140	1,200	1,120	1,180	970	940
Residual magnetism ...	400	420	350	350	380	390	590	600
Coercive force	8·5	9·0	6·0	6·0	7·0	8·0	35	40

TABLE VII.

Whitworth Chrome Steel, 4 per cent. Cr.

Composition.	C, 0·50 ; Mn, 0·50 ; Si, 0·29 ; Cr, 4·07.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	3	2	3	2	3	2	2	1
1	5	4	7	5	6	5	4	2
2	10	9	17	12	12	10	8	6
3	15	13	25	18	21	18	12	10
4	20	18	30	25	28	25	15	11
5	25	24	40	30	32	29	20	16
10	55	52	82	65	70	66	38	30
20	147	136	216	168	185	178	85	70
30	450	350	480	425	440	425	165	140
40	670	590	680	654	650	650	300	260
50	790	750	785	770	760	764	490	420
70	938	915	912	912	897	910	765	735
100	1,050	1,042	1,025	1,020	1,020	1,010	950	930
150	1,160	1,162	1,170	1,185	1,130	1,185	1,100	1,090
Residual magnetism ...	710	725	625	640	600	630	665	670
Coercive force	27	28	20	23	20	23	41	45

TABLE VIII.

Whitworth Silicon Steel.

Composition.	C, 0·35 ; Mn, 0·71 ; Si, 3·47.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	10	6	15	8	10	6	3	6
1	18	14	30	20	20	16	8	12
2	40	35	65	50	42	36	16	22
3	70	60	100	90	70	60	24	32
4	130	100	150	120	130	100	32	50
5	180	150	200	170	180	152	42	62
10	500	460	510	470	500	460	110	145
20	760	720	780	725	770	730	290	320
30	860	830	880	840	865	830	440	490
40	930	912	955	925	935	912	575	625
50	980	970	1,005	980	990	975	690	745
70	1,055	1,050	1,070	1,055	1,060	1,055	840	900
100	1,140	1,140	1,140	1,130	1,142	1,140	960	1,120
150	1,160	1,162	1,160	1,165	1,160	1,165	1,060	1,110
Residual magnetism ...	440	440	400	410	420	430	550	580
Coercive force	5	5	4	4	4	4	23	24

TABLE IX.

Whitworth Silicon Steel, 6 per cent. Si.

Composition.	C, 0·42 ; Mn, 0·71 ; Si, 6·07.							
Thermal Treatment.	Normalised.		Annealed at 900°C.		Quenched at 450°C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	16	9	25	16	16	9	12	8
1	30	16	60	30	20	10	30	20
2	110	60	130	80	110	60	80	40
3	410	180	450	210	200	155	160	80
4	520	310	570	320	520	310	290	120
5	570	450	620	460	580	460	370	180
10	750	700	780	720	760	710	580	500
20	890	865	890	850	896	870	770	790
30	960	920	950	920	970	940	872	892
40	1,010	980	990	965	1,016	990	950	972
50	1,040	1,018	1,030	1,000	1,045	1,020	1,000	1,020
70	1,075	1,062	1,090	1,062	1,082	1,066	1,070	1,092
100	1,125	1,122	1,140	1,130	1,130	1,122	1,140	1,160
150	1,185	1,190	1,190	1,190	1,190	1,190	1,180	1,200
Residual magnetism ...	350	350	230	380	200	300	200	320
Coercive force	3·0	5·0	2·0	3·0	2·0	3·5	2·0	3·5

TABLE X.

Whitworth Phosphor Steel, 0·168 P.

Composition.	C, 0·47 ; Mn, 0·17 ; Si, 0·27 ; P, 0·168.							
Thermal Treatment.	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	15	12	18	15	12	9	4	3
1	30	24	30	25	30	20	8	5
2	70	60	70	60	70	50	15	10
3	115	100	120	100	140	100	20	15
4	185	140	190	150	220	150	28	20
5	230	195	240	200	300	250	35	27
10	480	390	550	480	650	550	70	55
20	760	640	800	710	830	730	155	125
30	910	790	915	845	930	850	290	225
40	980	930	980	930	1,110	940	490	360
50	1,020	970	1,030	990	1,065	1,110	670	530
70	1,100	1,080	1,110	1,080	1,135	1,105	860	770
100	1,170	1,180	1,200	1,180	1,210	1,200	1,000	840
150	1,270	1,280	1,300	1,280	1,280	1,295	1,090	1,040
Residual magnetism ...	570	570	480	480	400	550	650	670
Coercive force	5·0	5·0	3·5	4·0	3·5	4·0	33	40

TABLE XI.

Whitworth Tungsten Steel.

Composition.	C, 0·51 ; Mn, 0·13 ; Si, 0·19.							
Thermal Treatment	Normalised.		Annealed at 900° C.		Quenched at 450° C.		Quenched at 900° C.	
Temperature of Test.	15° C.	−190° C.	15° C.	−190° C.	15° C.	−190° C.	15° C	−190° C.
H.	I.	I.	I.	I.	I.	I.	I.	I.
0·5	2	1	2	1	2	1	2	1
1	3	2	5	3	3	2	3	2
2	10	8	11	8	11	7	4	3
3	16	13	22	18	20	17	6	4
4	28	20	37	30	36	30	8	6
5	35	30	53	42	52	42	11	8
10	130	110	200	150	200	150	32	23
20	610	450	610	540	560	510	93	67
30	830	750	830	760	770	740	192	130
40	900	870	915	880	895	865	335	225
50	960	940	980	950	970	950	510	340
70	1,060	1,045	1,070	1,050	1,052	1,040	800	655
100	1,145	1,140	1,150	1,145	1,130	1,128	950	862
150	1,210	1,215	1,215	1,220	1,220	1,220	1,015	1,070
Residual magnetism ...	745	760	540	600	570	570	610	650
Coercive force	12·5	15·0	10·0	12·5	7·5	7·8	37	45

sive. Magnetisation curves for high carbon steel and one of the chrome steels are exhibited in Figs. 2 and 3.

Discussion of the Results.

Carbon Steels.—In Swedish soft iron and carbon steel the effects of cooling the specimens to — 190° C. are quite normal, that is, the permeability is reduced for low and medium values of the magnetising force, and augmented for very high values. In the case of the mild steel crossing of the magnetisation curves corresponding to 15° C. and — 190° C. takes place for a value of H of about 170 c.g.s. units for all four conditions of the metal. As the carbon content increases the value of the magnetising forces necessary to bring about crossing of the curves, rises. This holds for all conditions of the material.

In these steels the effect of the low temperature is in general to bring about an increase in the coercive force ; in the annealed condition of the material the increase is slight, but it is very great in the case of high carbon steel after quenching at 900° C.

Sankey Transformer Iron.—Specimens of this material were examined in the annealed and case-hardened conditions. By the process of case-hardening soft iron is converted into high carbon steel. Dewar and Fleming found for this material that the effect of cooling a specimen in liquid air was to bring about a large increase in the permeability for all values of the magnetising force. Our experiments do not confirm this result : the metal in both conditions behaved normally.

Chrome Steels.—The results yielded by the specimen containing 1 per cent. Cr, are remarkable for the fact that in conditions 3 and 4 of the material crossing of the magnetisation curves corresponding to 15° C. and — 190° C. takes place for a very small value of the magnetising force. The curves for the annealed and quenched conditions are shown in Fig. 3. It will be seen that for the former condition of the metal the curves cross for H = 8 c.g.s. units. For a value of the magnetising force of 150 c.g.s. units the intensity of magnetisation at room temperature is 1,140 ; at — 190° C. it is 1,200.

The behaviour of the material after quenching at 450° C. is very similar to that which it exhibited in the annealed condition. After quenching at 900° C. its properties are entirely altered : the magnetisation curve corresponding to — 190° C. is now everywhere below that corresponding to room temperature ; the curves show, moreover, that a very large value of the magnetising force would be required to bring about crossing.

The effect of the low temperature is to increase the coercive force and the residual magnetism.

The results yielded by the chrome specimen containing 4 per cent. Cr are very similar to those which were obtained in the case of the specimen containing the lower percentage of chromium. In the annealed condition of the material crossing of the curves takes place for a value of H of 70 c.g.s. units. For the quenched material the curve corresponding to —190° C. is everywhere below that corresponding to room temperature.

Silicon Steels.—These steels exhibit high permeability and small coercive force in all five conditions. Their behaviour in all five conditions at the temperature of liquid air is remarkable in some respects. The specimen containing 3 per cent. Si on being tested in the annealed condition gave normal results ; crossing of the curves took place for a value of the magnetising force of 150 c.g.s. units. In this condition of the metal the coercive force at both temperatures was 4. After quenching at 900° C. the magnetic properties underwent a very marked alteration. The magnetisation curve

at —190° C. was now found to be everywhere above that corresponding to room temperature. Furthermore, the coercive force at the two temperatures had become 23 and 24 respectively.

In the case of the specimen containing 6 per cent. Si, crossing of the curves took place, for the annealed condition of the material, at a value of the magnetising force of 150 c.g.s. units. In the quenched condition of the specimen the curves crossed for H = 8 c.g.s. units. In both the silicon steels tested, therefore, the effect of quenching is to lower the value of the magnetising force necessary to bring about crossing of the curves.

Phosphor and Tungsten Steels.—The behaviour of these steels was quite normal and calls for no special comment. Tungsten steel is magnetically much harder at —190° C. than at 15° C.

The experiments above described show the necessity for carrying out further work on chrome and silicon steels. Tests carried out on a graded series of these steels at different temperatures would in all probability yield results of a very interesting character. Further study of the effects of quenching on the magnetic properties of materials is necessary. As has already been pointed out, quenching is an uncertain process, as the outer portions of a test-piece cool much more rapidly than the inner. The authors are at present engaged upon a series of quenching tests in which the specimens are in the form of tubes, and the results are very promising.

The work just described was carried out in the Natural Philosophy Institute of the University of Glasgow. The cost of the materials was defrayed from a grant put at the disposal of the Department of Natural Philosophy by the Bellahouston Trust, to whom the authors desire to take this opportunity of expressing their thanks.

Summary.

1. Specimens of iron, carbon steels, chrome steels, silicon steels, phosphor and tungsten steels were tested at room temperature and at — 190° C. (when immersed in liquid air) in the conditions brought about by—

(1) Normalising.
(2) Annealing at 900° C.
(3) Quenching at 450° C.
(4) Quenching at 900° C.

2. The effect of cooling to the temperature of liquid air is in general to diminish the permeability for low values of the magnetising force, and to augment it for high values. A magnetisation curve corresponding to — 190° C. lies initially below and finally above that corresponding to room temperature.

3. In the carbon steels the value of the field strength for which the curves cross increases with the carbon content. In these steels the coercive force is greater at — 190° C. than at 15° C. In high carbon steel in the quenched condition the coercive force is 32 at room temperature ; at — 190 ° C. it is 50.

4. The crossing points of the curves are very low in the case of chrome steels. In annealed steel of this variety containing 10 per cent. Cr the crossing point is at H = 8, and is only slightly higher in the condition brought about by quenching at 450° C. In this steel cooling to — 190° C. brings about an increase in the coercive force.

5. In annealed steel containing 4 per cent. Cr, crossing of the curves takes place for H = 150. In the condition brought about by quenching at

450° C., crossing takes place at H = 16. Quenching at 900° C. results in the magnetising force necessary to bring about crossing becoming very great.

6. In annealed silicon steel containing 3·5 per cent. Si, crossing of the curves occurs for H = 150 c.g.s. units. After quenching at 900° C. the magnetisation curve corresponding to — 900° C. lies everywhere above that corresponding to room temperature.

7. An annealed steel specimen containing 6 per cent. Si behaved in a somewhat similar manner. In the annealed condition of the material crossing of the curves took place for H = 180 c.g.s. units. After quenching at 900° C. crossing took place for H = 15 c.g.s. units.

8. In the silicon steels the effect of the liquid air temperature is to increase the coercive force.

9. Specimens of tungsten and phosphor steels behaved quite normally. Tungsten steel is magnetically much harder at — 190° C. than at ordinary room temperature.

10. In all cases where a series of special steels has been examined the general rule is found to hold that the crossing point of the I–H curves corresponding to 15° C. and — 190° C. respectively is higher the greater the amount of the added element—carbon, silicon, chromium, etc. This rule holds for the steels in any of the conditions—normalised, annealed or quenched.

THE MAGNETIC PROPERTIES OF NICKEL AND MANGANESE STEELS WITH REFERENCE TO THEIR METALLOGRAPHIC CONSTITUTION.

A Paper by **Dr. E. Colver-Glauert** (Sheffield) and **Dr. S. Hilpert** (Berlin) on "The Magnetic Properties of Nickel and Manganese Steels with Reference to their Metallographic Constitution" was read by Dr. Colver-Glauert.

The study of the magnetic properties of iron and its alloys has for a long time been one with a great fascination for metallurgists, and various theories have been put forward at different times in explanation thereof. One which has obtained wide credence is known as the allotropic theory, and assumes that at different temperatures iron undergoes allotropic modification, resulting in the production of materials with differing properties. If this theory be correct, it presents a very simple explanation of many curious phenomena, but in the authors' opinion it is untenable.

Broadly speaking, the allotropic theory states that below 750° C. iron exists in the Alpha condition and is magnetic and soft, that at this temperature it changes into the Beta variety, which is unmagnetic and hard, and at 900° C. it changes into the Gamma variety, which is equally unmagnetic but soft. It is stated that these varieties of iron may be preserved at room temperatures by a rapid quenching from the temperatures at which they are stable, and that the positions of the change points are modified by other elements which may be alloyed with the iron, to such an extent in certain cases that the Beta and Gamma varieties are stable at room temperatures. Following this it is assumed that all magnetic steels consist solely of Alpha iron, their properties resting entirely on their Alpha iron contents, and that all unmagnetic steels contain only Beta or Gamma iron. Similarly, the hardening of steels is alleged to be due to the conversion of Alpha into Beta iron.

The method usually adopted for estimating the magnetic change-point (Alpha $\rightleftharpoons$ Beta) is to heat a piece of iron in proximity to a magnetic needle and to note the temperature at which the latter is no longer attracted by the iron, but assumes the N. to S. direction. That this method is inaccurate is readily seen when it is understood that all that is really shown is the point at which the magnetism induced in the iron by the weak field exerted by the needle is less than that of the earth's field. Osmond investigated his nickel steels by this method.

The pioneer work on nickel steels was conducted by Professor Hopkinson, who communicated his results to the Royal Society in 1899 and 1900. The work was done by a quantitative method, and proved that in the case of iron containing 25 per cent. of nickel the temperatures at which the alloy became unmagnetic and regained its magnetism were separated by several hundred degrees.

Contrary to Hopkinson, Osmond, as stated above, employed only a qualitative method. He investigated a very complete series of alloys, and took considerable care in their preparation and treatment, whereas Hopkinson's

steels were practically as delivered by the makers, being treated purely from a physicist's standpoint, and according to metallurgists' views thereby losing much value. Nevertheless, Hopkinson's results remain as the only ones which have not been proved false by subsequent work.

From the results he obtained Osmond published the diagram reproduced in Fig. 1, to which the authors have added the freezing-point curve. In the

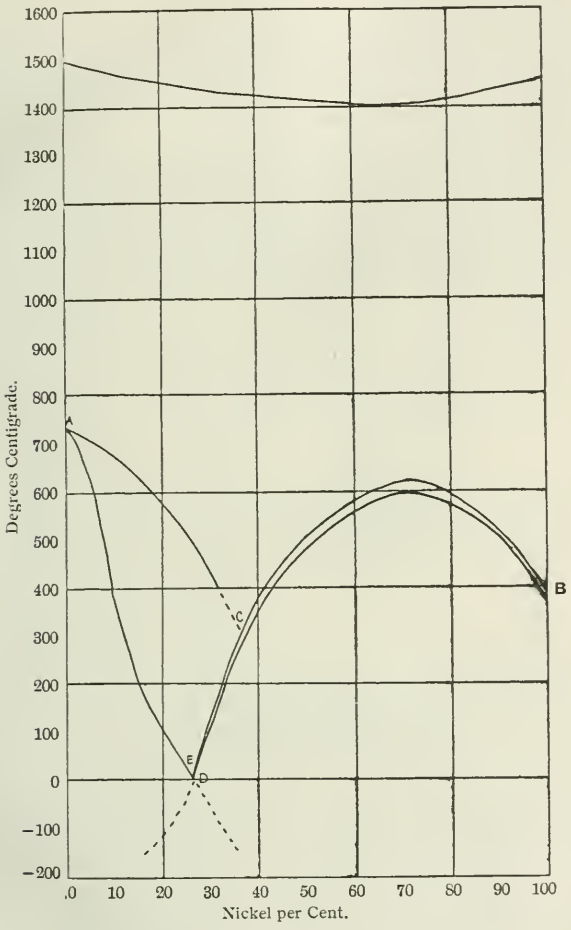


Fig. 1.

lower part of the diagram the lines *A* to *C* and *E* to *B* show the temperatures at which the alloys lose their magnetic properties on heating, and the lines *ADB* the temperatures at which these are regained on cooling. This shows that with increasing percentages of nickel an increasing temperature-hysteresis is found, reaching a maximum with about 27 per cent. of nickel, above which percentage the transformation is reversible. If the allotropic theory be accepted as correct a very simple explanation of these curious phenomena is to hand, namely, that above *ACEB* only Gamma iron exists, below *ADB* only Alpha iron, whilst in the area enclosed by *ACDA* either is stable.

Similar phenomena to the above are observed in manganese steels, as first proved by the work of Sir Robert Hadfield.

Despite the enormous amount of research which has been done on these alloys, their properties are as yet by no means clearly understood. Even if iron is allotropic, and a given modification is unmagnetic at the temperature at which it is formed, it certainly does not follow that it is also unmagnetic when not at temperatures at which it is in a stable condition, for example, at normal room temperatures.

One method of investigating this subject is rapidly to quench the steels from various temperatures, and then estimate their magnetic properties at room temperature by a quantitative method. This was the method adopted by the authors for the present research.

The authors selected a series of alloys which, according to previously published researches, led one to expect a very typical steel from each part of the diagram to be included, and which have been considerably used in previous investigations of the magnetic properties of the systems and in connection with their allotropic modifications.

Table I. gives the analyses of the alloys employed :—

Table I.

Steel No.	Nickel.	Manganese.	Carbon.
	Per Cent.	Per Cent.	Per Cent.
1	5·86	0·20	0·37
2*	12·60	0·45	0·21
3	20·10	0·51	0·18
4	24·32	0·76	0·24
5†	27·35	0·64	0·20
6*	32·90	0·70	0·21
7*	—	4·58	0·27
8*	—	11·67	0·29
9*	—	11·80	1·33
10*	—	11·70	2·18

* In collaboration with W. Mathesius.
† In collaboration with W. Kohl.

The thermal treatment of the steels was carried out in a Heræus electric furnace. A finished magnetic test bar and a microsection from each steel were suitably fastened together and placed in the glazed porcelain tube. An atmosphere of nitrogen was maintained during the whole of the treatment and effectively prevented oxidation of the test pieces. The furnace was maintained at the desired temperature for at least a quarter of an hour, and then, in the case of the quenched specimens, one end of the tube was opened, and all the pieces pulled out together by means of a piece of wire previously attached and allowed to fall into a large tub of iced water, which was vigorously stirred. In the case of those test pieces which were to be slowly cooled, the current was switched off after the initial temperature had been maintained for a quarter of an hour and the pieces allowed to cool in the furnace, a slow stream of nitrogen being passed through all the time, cooling being complete in about eight hours.

When subjecting the specimens to temperatures below zero, the test piece and corresponding microsection were placed in one of the usual double-walled receptacles, maintained at the desired temperature for ten minutes,

and then allowed to regain room temperature. For temperatures down to — 50° C. alcohol cooled with liquid air was used, between here and — 120° C. the alcohol was replaced by petrol ether, and for the treatment at — 180° C. the pieces were placed in boiling liquid air, which maintained the temperature constant within 2° of the desired point.

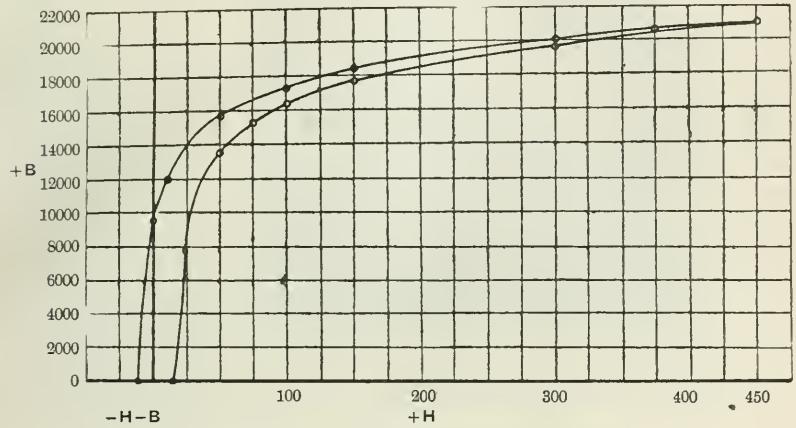


FIG. 2.—5 per cent. Nickel quenched from 600° C.

The strongly magnetic steels were measured in the Du Bois magnetic precision balance, using bars 2π (6·3) centimetres long with ball ends. This size of test piece is very suitable for work of this nature, as the bars are not too long, so rendering the thermal treatment possible without giving rise to warping or variations in rapidity of quenching, &c. For those steels which

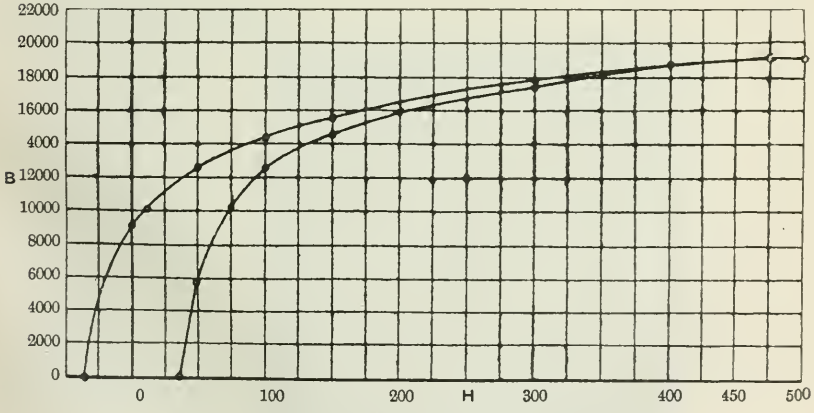


FIG. 3.—5 per cent. Nickel quenched from 900° C.

were only feebly magnetic it was found that the Du Bois balance was not sufficiently sensitive, and the authors constructed a ballistic installation using test bars of the same dimensions as the Du Bois balance the sensitivity of which could be varied over a very wide range, and this was found to be quite satisfactory, although, of course, the hysteresis loop could not be taken.

The metallographic examination was first made after the sections had been etched with the usual media, when the well-known structures of these alloys, consisting of so-called austenite, martensite, &c., were observed. On etching with an aqueous solution of sulphurous acid, used as described by the authors in the *Journal of the Iron and Steel Institute*, 1910, vol. ii., a totally different

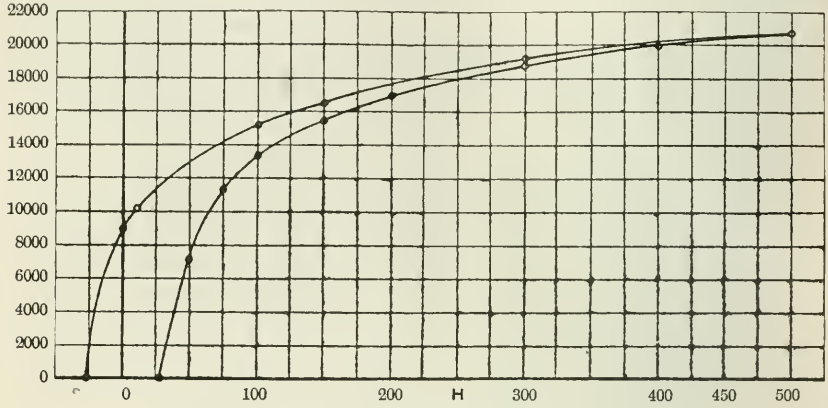


FIG. 4.—5 per cent. Nickel quenched from 1240° C.

series of structures were obtained, and it is the latter that are reproduced herewith. These structures approximate that of meteoric iron very closely.

Specimens of the 5 per cent. nickel steel were quenched from 600° C. 900° C., and 1,240° C., and slowly cooled from 1,250° C. The hysteresis

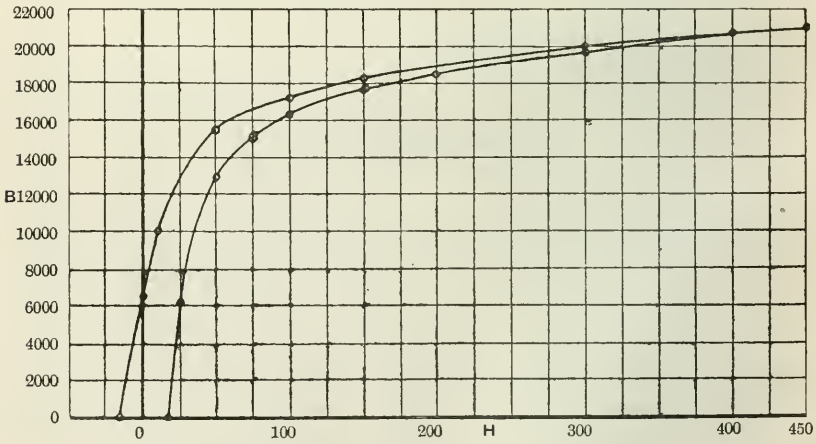


FIG. 5.—5 per cent. Nickel slowly cooled from 1250° C.

curves from these as obtained in the Du Bois balance are reproduced in Figs. 2, 3, 4, and 5 respectively. The magnetic properties of the bars quenched from 600° C. and slowly cooled are practically the same, but it is apparent that quenching from 900° C. produces a considerably harder material, since in this specimen the magnetisability is at a minimum and the coercive force at a maximum. Quenching from 1,240° C. gives rise to a

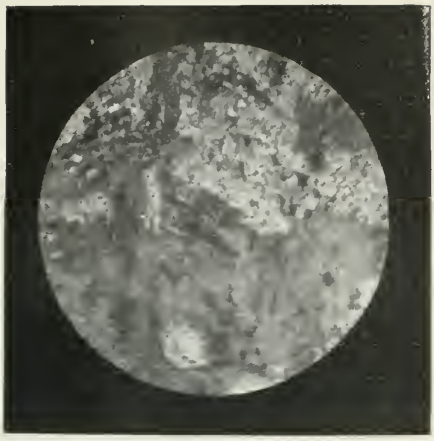


FIG. 6.

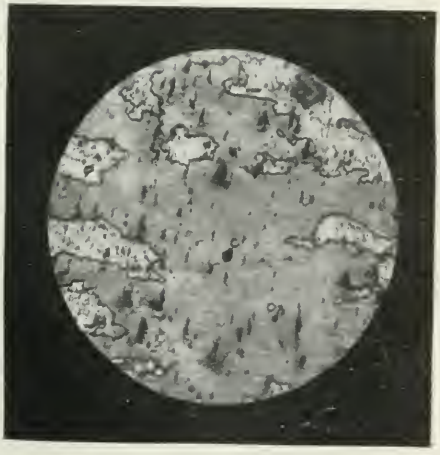


FIG. 22.

material which is much softer than the last, and is practically as strongly magnetic as the slowly cooled specimen, although according to the allotropic theory the latter should consist entirely of Alpha iron, whilst the former was

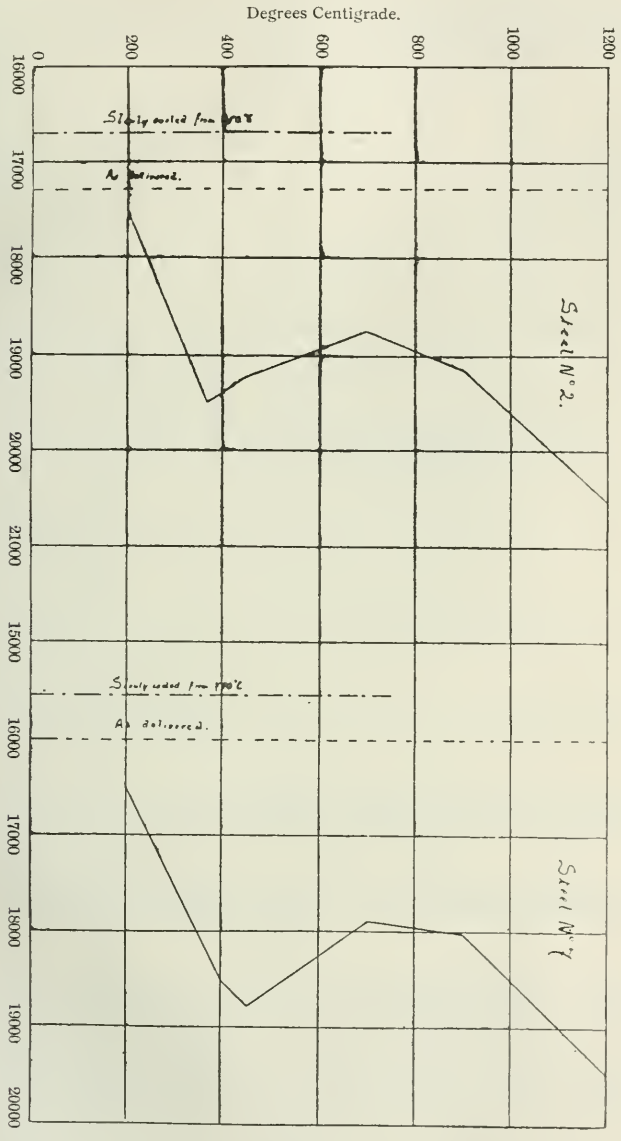


FIG. 7.

quenched from a temperature well within the area of stability of the alleged Gamma iron.

Metallographic examination showed that the steel when slowly cooled or quenched from 600° C. consists of ferrite and pearlite, only varying in the degree of lamellation of the latter constituent. Quenching from 900° C. produces an entirely martensitic structure, whilst the specimen quenched

from 1,240° C. shows several constituents, one of which is martensitic, as shown in the photomicrograph reproduced in Fig. 6 (facing p. 138).

The steels containing 12 and 20 per cent. nickel and 5 per cent. manganese exhibit very similar properties to the above. The results for a series of quenchings are depicted graphically in Figs. 7 and 8. In Fig. 7 the abscissæ denote the magnetisability at 800 c.g.s., whilst the ordinates show the

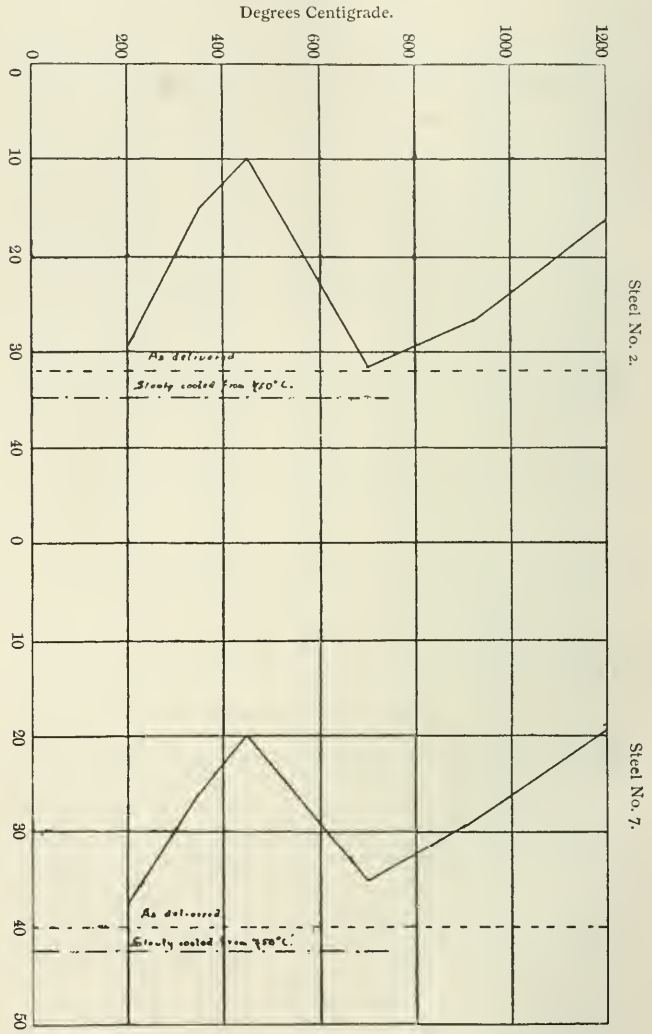


FIG. 8.

temperatures from which the specimens were quenched. The magnetisability rises until the quenching temperature reaches 450° C., sinks as the temperature rises to 900° C., and reaches a maximum by quenching from 1,200° C. Against this the slowly cooled material is the weakest magnetically. The coercive force is influenced in an exactly opposite manner, that is, when the magnetisability is at a maximum the coercive force is at a minimum, and *vice versa*. This is graphically depicted in Fig. 8, the abscissæ in this case

being coercive force. In these cases again it is obvious that the magnetic properties cannot be explained by the assumption that they are solely dependent on Alpha and Gamma iron, since they follow exactly the same order as those of the 5 per cent. nickel alloy.

Cooling below zero produced no change in the foregoing steels.

The 25 per cent. nickel steel was, on account of its most remarkable properties, the one to which the authors have devoted most attention and on which by far the greatest amount of work has been done.

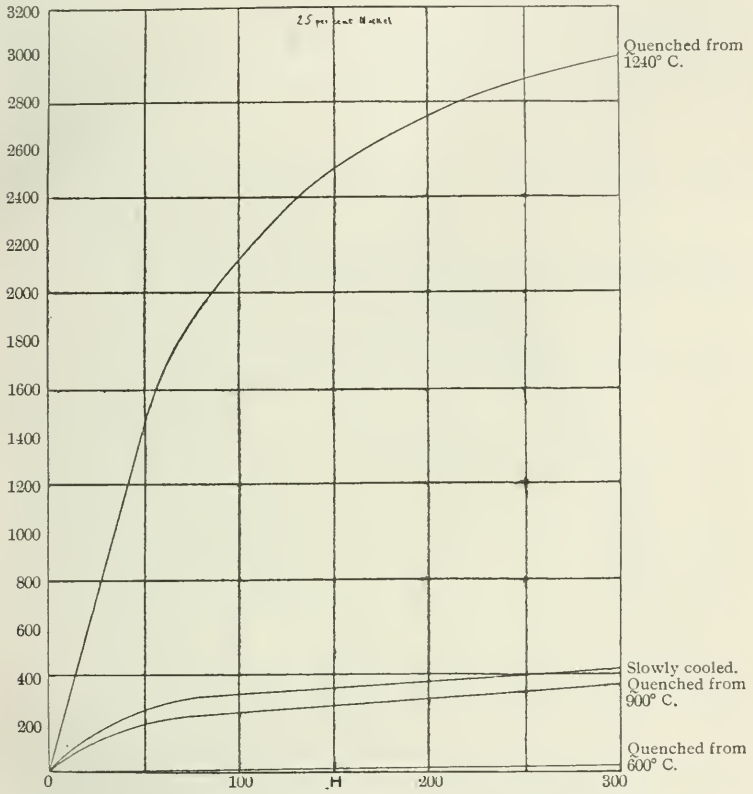


FIG. 9.

Preliminary experiments were made by quenching specimens from 600°, 900°, and 1,240° C., and by slowly cooling from 1,250° C. It was in the case of these test bars that the authors first found that the Du Bois balance could not be used, and they were therefore constrained to use the ballistic installation. The curves obtained from these specimens are shown in Fig. 9. It will be seen that the thermal treatment has had a most marked effect on this steel. Whilst the specimen quenched from 600° C. is practically unmagnetic, the one quenched from 900° C. is already measurable, and could indeed be moved with a weak horseshoe magnet. Quenching from 1,240° C. has, however, had a most remarkable effect, and has produced a material approximately one-seventh as magnetic as pure iron. The slowly cooled specimen is also comparatively strongly magnetic. The authors would again point out that the results shown by this steel are in no way

compatible with the allotropic theory; in fact, if that theory were correct it would appear that the magnetic order of the test bars would be the exact opposite to that found. In connection with these preliminary experiments the above specimens were next cooled to —50° C., —100° C., and —180° C., magnetic measurements being taken at room temperature after each step. This showed that there is no sudden change at a definite temperature upon which the material suddenly becomes completely magnetic (Hopkinson shows a complete change at —52° C., and Guillet at 0° C.), but that as the temperature is lowered the magnetisability is gradually increased. Whether this change is complete at —180° C. or not, the authors are at present unable to state, since at the time of conducting the present research this was the lowest

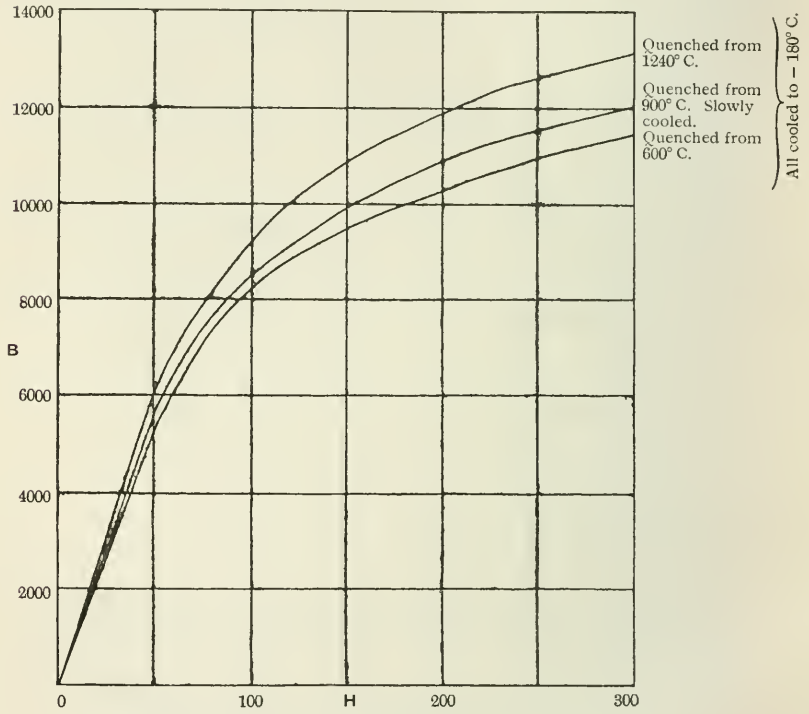


Fig. 10.

temperature they were able to produce, considering the comparatively large size of the test bars being used, but they hope in the near future to have access to a considerable quantity of liquid hydrogen, and will then investigate the steels in a still lower range of temperature. This treatment showed that the cooling did not transform all the materials produced by the previous thermal treatment into one common material, since the specimen originally quenched from 1,240° C. remains stronger than the others by practically the original difference, and though the bars quenched from 900° C. and slowly cooled now coincide, they are still in advance of the one quenched from 600° C. Ballistic curves obtained from the steel thus treated are shown in Fig. 10. In this state the steels were of course measurable in the Du Bois balance, and in order to show the type of curve possessed by the steel, Fig. 11 is reproduced, and depicts the hysteresis loop of the bar quenched from

1,240° C. after being cooled to —180° C. It will be seen that the type of curve is that of a very hard material and that even at a field strength of 450 the material is by no means saturated. (The saturation point of iron is about 130.) Another remarkable point in this curve is the high value of the coercive force, although the retentivity is only low.

The products were now carefully heated in a non-oxidising atmosphere in an electric furnace, the progression being made by steps of 50° C., the bars being tested, at room temperatures, after each step. This proved that heating up to 450°C. results in a slight gradual increase in the magnetisability, above which temperature it falls away fairly rapidly, reaching a minimum which is practically zero at 700°C. In this neighbourhood the authors found considerable difficulty in obtaining concordant results, as totally different products were apparently produced if the bars were removed and quenched on a heating or cooling curve, and this will be readily understood when the peculiar behaviour of the steel in this region of temperature is explained later. On continuing the heating above 700°C. the magnetisability again

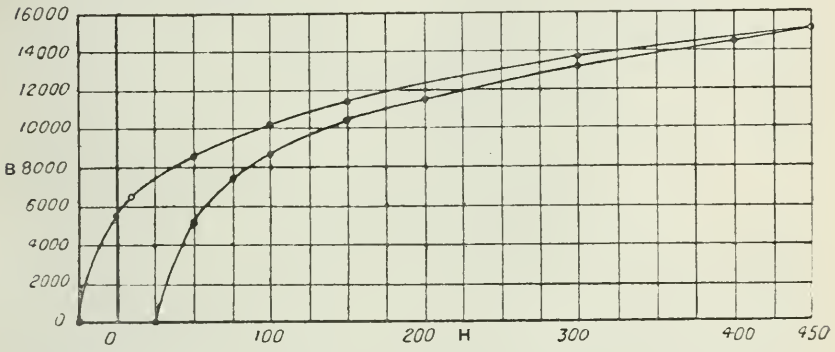


Fig. 11.—25 per cent. Nickel quenched from 1240° C. Cooled to — 180° C.

rises, reaching a maximum at 950°C., falls again with a minimum at 1,050°C., and after this point continues to rise gradually, at least to the top limit of the author's investigations, viz. 1,240°C.

It has been shown that if this steel be quenched from 600°C. (not having been previously heated much above this point) or about 750°C. it is unmagnetic, but if quenched from or above 900°C. it is magnetic, and it might therefore be assumed that a change-point or line of stability exists in this region, above which there is a magnetic product and below which an unmagnetic one; but if this were the case a slowly cooled steel must necessarily be unmagnetic, whereas the opposite is the case. In all specimens of the steel which were slowly cooled the same fairly high degree of magnetisability was found. The curve between 450°C. and 950°C. was next very carefully investigated, and it was found that on quenching or slowly cooling the steel from any given point on this curve the same degree of magnetisability was retained, whilst all specimens slowly cooled from above 950°C. exhibited the maximum. From this it was only possible to assume that a second irreversible temperature-hysteresis loop existed here, and in order to ascertain that no mistake had been made the experiments were repeated several times.

The whole series of experiments were now repeated, with the interpolation

of many new stages, both above and below zero, and finally the authors were able to construct a diagram showing the complete changes which this steel undergoes between the limits of 1,240° C. and — 180° C. This is reproduced in Fig. 12. The lower temperature-hysteresis loop of this diagram is essentially the one discovered by Hopkinson, with the exception of such details as regards temperature of changes and completeness thereof which have been previously noted. The upper temperature-hysteresis loop accounts for the difficulties experienced by the authors in their preliminary experiments, and it will be understood that the steel must follow the curved line to the

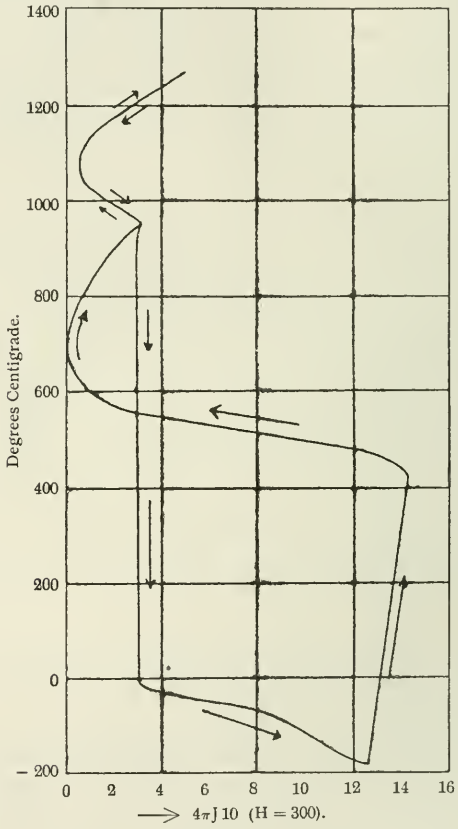


FIG. 12.

left on heating and the straight line to the right on cooling. The steel, when cooled slowly from a high initial temperature, must follow the vertical line from 950° C., but a steel cooled from any intermediate point will cool along one of an infinite number of vertical lines from any point on the curve between 550° C. and 950° C. The only means by which the steel may be rendered totally unmagnetic is by quenching or cooling from 700° C. when this point is reached on heating. Above 900° C. the changes are reversible ; that is, the same line is followed both on heating and on cooling.

Metallographic examination of this steel after the various thermal treatments described showed that by etching with sulphurous acid very different structures were developed from those produced by the more generally employed

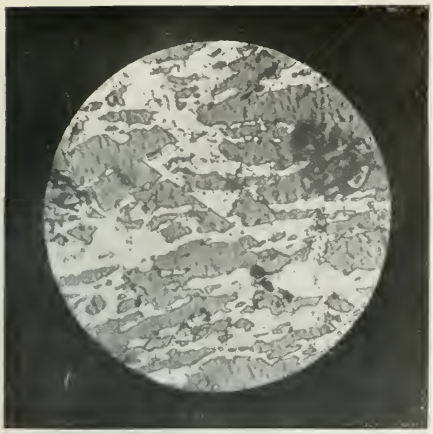


FIG. 13.

FIG. 14.

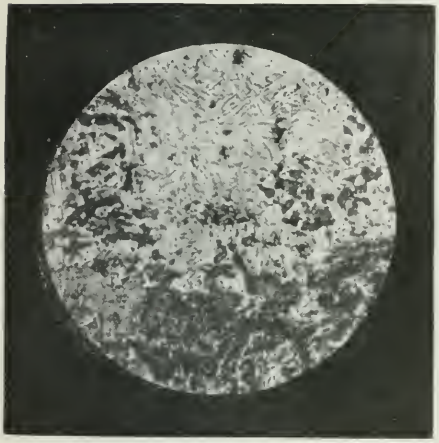


FIG. 15.

FIG. 16.

FIG. 17.

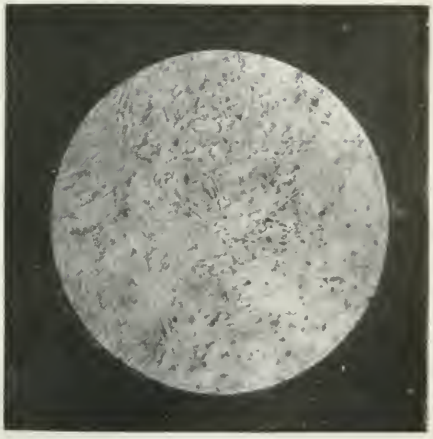


FIG. 18.

media. Typical photomicrographs are reproduced herewith (facing p. 144). Fig. 13 depicts the structure of the specimen when quenched from 600° C., and is also typical of others up to 900° C. Three constituents are visible—one pale etching, one darker, and the third occurring as thin dark bands between the other two. Fig. 14 shows the structure obtained on quenching from 1,240° C., and is of a very similar type to that of the previous specimen. Fig. 15 is the structure of the slowly cooled specimen, and it is observable that in this case one of the constituents is martensitic in nature. The presence of several constituents in these structures is somewhat remarkable, since, according to the freezing-point diagram of this series of alloys, only mixed crystals occur, which should produce a homogeneous structure. A structure more after this nature is obtained on etching with an electrolytic medium, and has frequently been depicted and called austenite. Against this, however, may be noted the structure of those meteoric irons consisting of a nickel iron alloy, which almost invariably show several constituents on being etched. As to the reason for the different etching effects obtained of these alloys, the authors can only state that they are still of the opinion that their medium is purely chemical in its attack and therefore only differentiates constituents with differing chemical composition, whereas the electrolytic media differentiate by the potential of the constituents, and it is quite possible for various parts of the same compound to have different potentials, due possibly to molecular orientation, or for different compounds, under certain conditions, to possess similar potentials. Further, it is possible that during its life as a meteorite the nickel iron alloy undergoes some change whereby its constituents assume different potentials, thus enabling them to be developed by electrolytic media, and that the time factor of this change is so great that it is impossible of artificial reproduction. On subjecting the specimens to a temperature of — 50° C. the structures become more martensitic, and this development may be observed without further etching, as it stands out in relief, as shown by Fig. 16, which may be regarded as typical of the set. The appearance on re-etching is shown in Fig. 17. Cooling to — 100° C. renders the material completely martensitic, as depicted in Fig. 18, which shows a section after re-etching. Further cooling produced no further change in these structures, although a very marked change in the magnetic properties occurs below this point. The martensitic structure remains unchanged during the subsequent heating until the unmagnetic zone is reached, when there is a sudden re-appearance of the original structure as depicted in Fig. 13.

These results, when considered in relation to the magnetic properties, are so widely divergent that the authors are unable to observe any real connection between the two. The slowly cooled specimen originally possessed a partly martensitic structure, although it was considerably less strongly magnetic than the one quenched from 1,240° C., which was not at all martensitic. Neither was the slowly cooled specimen as strongly magnetic as the latter when both had been rendered completely martensitic by cooling. Thus steels with similar structures have very different magnetic properties and some with different structures have similar properties, whilst marked magnetic changes may take place in the material without the structure showing any change whatever.

The 27 per cent. nickel steel was found to be very similar in its properties to the 25 per cent., but the authors were unable to find the upper temperature-hysteresis loop (Fig. 12) found in the latter alloy.

The 10 per cent. manganese steels were found to possess very similar properties to the irreversible nickel steels.

In connection with these nickel steels the authors had considered that the

relatively high magnetisability possessed by them when quenched from high temperatures must be due to the formation at that temperature of a strongly magnetic compound which persisted through all subsequent treatments, and they were able to find conclusive proof of this in the manganese steels. Steel No. 8 showed this very clearly in specimens quenched from 1,200° C. Fig. 19 is a diagram showing the changes occurring in this steel during thermal treatment. The left-hand curve shows the magnetic properties when slowly cooled from 700° C., whilst the right-hand one depicts the behaviour of the steel when quenched from 1,200° C. This diagram shows that at least two constituents must be present, of which only one undergoes any change by

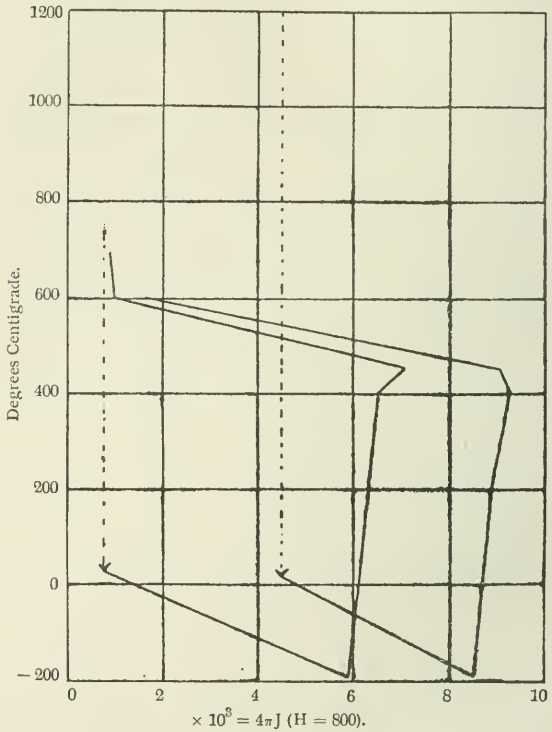


Fig. 19.

cooling to — 180° C., and further, that the constituent produced by quenching from 1,200° C. must be *per se* strongly magnetic.

Steel No. 9, containing 1 per cent. of carbon, shows this even more markedly. This greater difference is clearly shown by the diagram Fig. 20, depicting a similar set of treatments to Fig. 19. This enhanced difference may possibly occur because in the slowly cooled steel the carbide is present as free carbide and is not changed by the treatment in liquid air, whereas in the specimen quenched from 1,200° C. the carbide is dissolved in the iron and undergoes the change with the solute. Steel No. 10 (2 per cent. carbon) showed similar properties, but the difference between the two loops was even more marked.

The 33 per cent. nickel steel exhibits totally different properties from those of the steels previously considered. It is almost unaffected by thermal

treatment, and the question arises as to whether there is any connection between this fact and the proximity of the steel to Invar metal in composi

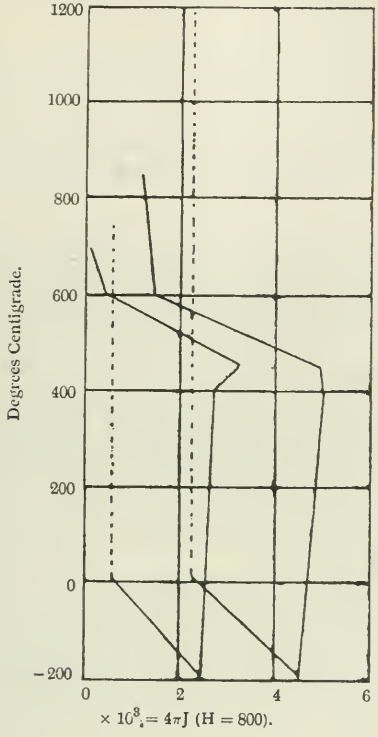


FIG. 20.

tion, the remarkable physical properties of the latter in regard to expansion under the influence of temperature being well known.

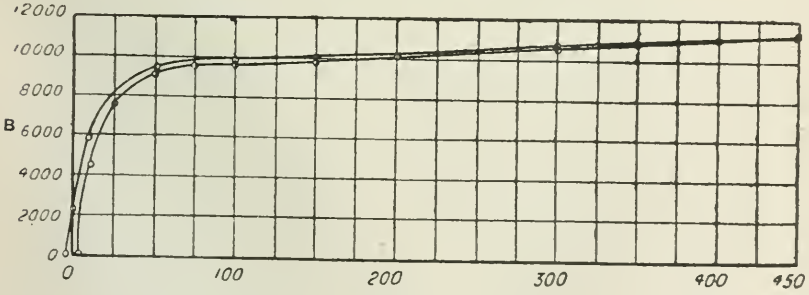


FIG. 21.—35 per cent. Nickel slowly cooled from 1250° C.

The slowly cooled specimen was the most strongly magnetic, and the magnetisability gradually decreased to a slight extent as the quenching temperature was increased to 1,240° C. The whole series, however, remain magnetically very soft, the coercive force being exceptionally small, the

saturation point low and with a fairly high retentivity, although the maximum induction is only about half that of pure iron. A typical curve as obtained by the Du Bois balance is shown in Fig. 21. The properties of this steel are so different from others of the series that it seems to be a definite and separate compound.

In the case of this steel metallographic examination showed the presence of several constituents, a typical structure being depicted in Fig. 22 (facing p. 138).

Neither the magnetic properties nor the metallographic structures of this steel were in any way changed on subjecting to cooling to — 180° C.

Conclusions.

After investigating a series of nickel and manganese steels with reference to the influence of thermal treatment on their magnetic and metallographic properties, the authors' main conclusions are :—

1. There is a distinct connection between thermal treatment and magnetic properties.

2. Any modification which is produced by quenching these alloys from 1,200° C. is in all cases, at room temperatures, strongly magnetic.

3. It is possible to define various constituents by their magnetic properties.

4. In the case of the 25 per cent. nickel steel two superimposed temperature-hysteresis loops exist.

5. A definite connection between metallographic structure and magnetic properties does not exist.

6. The metallographic structure of artificial nickel iron alloys closely approximates that of meteoric iron.

7. That the allotropic theory of the magnetic properties of iron alloys is not upheld by the facts.

THE MAGNETIC PROPERTIES OF THE ALLOYS OF THE FERROMAGNETIC METALS: IRON-NICKEL, NICKEL-COBALT, COBALT-IRON.

Professor Pierre Weiss, Professor of Physics at the Polytechnic School of Zurich, communicated a Paper entitled "The Magnetic Properties of the Alloys of the Ferromagnetic Metals: Iron-Nickel, Nickel-Cobalt, Cobalt-Iron."

The services which the examination of the magnetic properties has rendered to the study of the ferromagnetic alloys, and notably of the ferronickels, are generally recognised. In this short note I will not refer to the well-known results of the researches of J. Hopkinson, Osmond, Le Chatelier, Ch. Ed. Guillaume, Tammann, Guertler, and others. These results have, as a rule, simply been obtained by ascertaining the presence or absence of strong magnetism and the temperature ranges of these two states.

Several authors have recognised the necessity of supplementing the qualitative researches by quantitative determinations. This extension has, however, only become of real utility after a kinetic theory of magnetism* had thrown light on the meaning of the measured quantities, and had enabled us to recognise which properties are really characteristic. The scheme for magnetic researches which I outlined in 1909, together with novel experimental technics for this purpose,† aimed in particular at alloys which contain several distinct magnetic phases. The researches carried out in connection with this scheme have demonstrated that the metals hitherto examined are homogeneous solid solutions. At any rate, nothing characteristic has been revealed to indicate that they are not solid solutions, in spite of the great sensitiveness of magnetism in this respect. For instance, we have not found in the artificial ferronickels studied the constituents which form distinct and coexisting phases in the meteoric ferronickels: kamacite, taenite, plessite.

I will therefore point out the two magnetic quantities which are particularly characteristic for the solid homogeneous solutions. Theory gives the law of the variation of the saturation intensity of magnetism with temperature between absolute zero and the disappearance of strong magnetism or the Curie point. It shows at the same time that this saturation intensity has not in general any simple significance. The thermal agitation has the effect of inclining the molecular magnets more or less with regard to the direction of the magnetisation; the saturation intensity is hence not the sum of the molecular moments, but their resultant according to the parallelogram of forces, and it will be the smaller the more energetic the thermal agitation. At absolute zero, however, thermal agitation has ceased to exist. *At this*

* P. Weiss, *J. de Physique*, (4) 6, p. 666, 1907.

† Ibid., *Rev. de Métallurgie*, 6, p. 680, 1909; *Internat. Assoc. for Testing Materials*, Copenhagen, 1909, Paper vii, 2.

temperature limit then the saturation magnetism gives the true moment of the molecule.

For technical applications we have to consider the magnetic intensity I, or the induction B, as referred to the unit of *volume*. It is evident, however, that it will be better to introduce the moment of the unit of mass when we have to deal with chemical problems :—

$$\sigma = I/D$$

where D is the density. When we multiply this quantity by the gramme-molecule m, or by the gramme-atom a, we find the moment of the molecule or of the atom : σ_m or σ_a ; by σ_o, σ_{mo}, σ_{ao} I designate these same quantities at absolute zero.*

In order to determine the magnetic moment of the atom, H. Kamerlingh Onnes and myself † have measured the saturation intensity of iron and nickel in liquid hydrogen at 20° abs. In most such experiments liquid air will suffice. In an important memoir, which I shall have to quote again, Sir Robert Hadfield and B. Hopkinson ‡ have recognised the preponderating significance of saturation ; they do not say, however, that it is only at extremely low temperatures that saturation acquires its full value.

The second characteristic constant of magnetic metals is furnished by the study of the feeble magnetism at temperatures above the Curie point. In order to understand the nature of this characteristic we should first consider a large category of bodies, which are in general not metallic, and whose coefficient of magnetisation (susceptibility referred to the unit of mass) is inversely proportional to the absolute temperature. This is the case of oxygen and of most of the salts of paramagnetic or of ferromagnetic metals in the solid or dissolved state. When we multiply this coefficient by the absolute temperature we obtain a constant C, which has been called the Curie constant. In substances of this type the orientation of the molecular magnets differs only to an extremely small extent from that which prevailed before the application of the field, that is, from absolute confusion. There can be no question, hence, of experimentally attaining the perfect parallelism which admits of determining the molecular moment. What the experiment refuses to yield is given by the kinetic theory, however, with the aid of the formula—

$$\sigma_{mo}^2 = 3RC_m,$$

where σ_{mo} indicates the moment of the gm.-mol., C_m the Curie constant, and R the gas constant, the latter two magnitudes being referred to the molecular mass. The determination of the Curie constant is hence equivalent to the determination of the magnetic moment of the molecule or of the atom.

In the case of ferromagnetic substances at temperatures above the Curie point, the kinetic theory supplies me with the relation—

$$C_m = \chi_m (T - \theta),$$

where χ_m is the coefficient of magnetisation referred to the molecular mass, θ the temperature of the Curie point, and T the temperature of the experiment. C_m is nothing but the Curie constant which the substance would have

* From the moment of the gm.-mol. we pass to the moment of the mol. itself by dividing by the very large number of true molecules in the gm.-mol. This, however, is not necessary for our purpose.

† P. Weiss and H. Kamerlingh Onnes, *Comm. Phys. Labor. Leiden*, No. 114 ; *J. de Physique*, (4), 9, p. 555, 1910.

‡ R. Hadfield and B. Hopkinson, "The Magnetic Properties of Iron and its Alloys in Intense Fields," *J. Inst. E.E.*, 46, p. 235, 1911.

if it were to become paramagnetic by the suppression of actions between the molecules. C_m can in fact be expressed with the aid of the molecular moment by the relation which has already been indicated for the paramagnetic bodies—

$$\sigma_{mo}^2 = 3\,RC_m.$$

The linear variation of $1 : \chi_m$ with temperature has been observed in a great number of cases and within temperature intervals of several hundred degrees. It yields one of the most eloquent confirmations of the kinetic theory of ferromagnetism. The observation of the feeble magnetisation above the Curie point likewise, therefore, yields the magnetic moment by the intermediation of the constant C_m.

All the magnetic measurements of which I avail myself finally lead to the molecular moments in the case of pure metals. We have now to see what these measured quantities become in the case of homogeneous solid solutions. The saturation intensity at very low temperatures is by its very nature additive; it is equal to the sum of the magnetic moments of all the molecules, whether of the same or of different nature. The saturation intensity at very low temperatures will hence vary as a linear function of the composition of the alloy.

The case of the Curie constant is a little less evident. To deal with it we have to bear in mind that each molecular magnet is, in the magnetic field, acted upon by a couple which does not depend upon the nature of the molecules in its neighbourhood. According to the kinetic theory it resists this couple by virtue of the energy of the thermal movement of rotation.* Now the law of equipartition teaches that this energy does not depend upon the nature of the surrounding molecules, which may be identical with the molecule in question or be of a different nature. Each molecule, therefore, contributes in some way individually to the magnetisation and consequently to the Curie constant. In the solid solutions the Curie constant will therefore vary as a linear function of the composition of the alloy.

The Magneton.—The knowledge of the magnetic moments of the molecules lends greater importance to a curious property which I have recently discovered.† When we measure the magnetic moment of the same atom in all the conditions in which it is possible to obtain it, at very low and at high temperatures, and then in the various combinations of this magnetic atom with diamagnetic atoms (whose diamagnetism is negligible), we are at first surprised to obtain very different molecular moments. We understand afterwards that all these diverse moments have a common measure. Thus the atom of nickel has, at absolute zero, the moment $3 \times 1123{\cdot}5$; above the Curie point the moment is $8 \times 1123{\cdot}5$ over a range of 500°; at still higher temperature the moment becomes $9 \times 1123{\cdot}5$; in nickel salts finally the moment is $16 \times 1123{\cdot}5$. When we similarly compare the very numerous values which the iron atom can assume, we find again that there is a common measure, and that *this common measure is the same as that which had been found for nickel.* This property is general. The moments of the atoms of cobalt, manganese, chromium, vanadium, copper, uranium, and other elements all contain that common measure 1123·5 which I have called the "magnétongramme," or briefly the magneton.

Iron-Nickel.—Fig. 1 shows the saturation magnetism and the Curie con-

* Compare the detailed memoirs as to the reason why the problem of statistical dynamics is reduced to these two terms.

† P. Weiss, Le magnéton, *Archives des Sc. phys. et nat.* (4), **31**, May, 1911; *J. de Physique* (5), **1**, pp. 900 and 965, 1911.

stants of the ferronickels as a function of their compositions. These are the specific quantities from which the molecular quantities can easily be deduced. The striking feature in the results is that they are represented by two broken lines which clearly prove the existence of the compound Fe_2Ni.

The specific saturations at low temperature have at my request been measured by F. Hegg.* He has ascertained that this quantity is not additive, but the true reason, the existence of the definite chemical combination, has only become revealed by the measurement of the Curie constants which I have made in collaboration with G. Foëx.† Our conclusion is this: the ferronickels form two uninterrupted series of solid solutions, the first between Fe and Fe_2Ni, the second between Fe_2Ni and Ni. The molecular magnetic

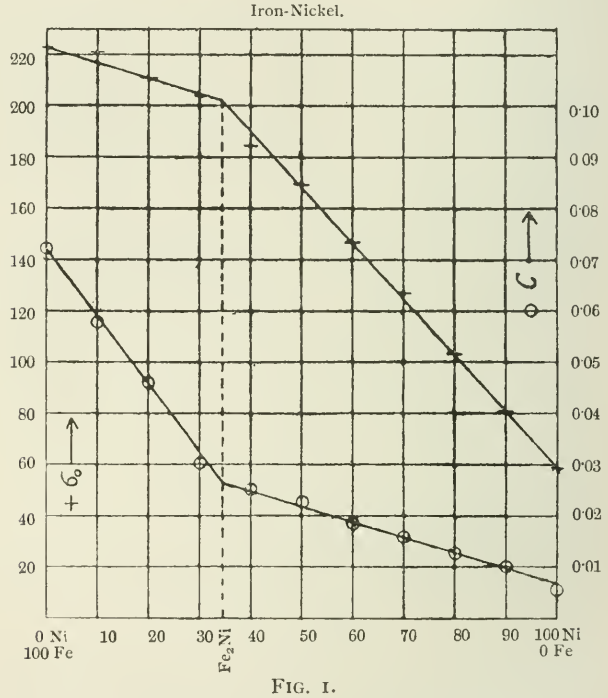


FIG. 1.

moment, which is additive in the solid solutions, ceases to be so in the chemical compounds.

Since then R. Hadfield and B. Hopkinson ‡ have re-observed this want of additivity in the saturation values at ordinary temperature and have noted it as a curious and unexplained fact: "This steel is remarkable in that its magnetism is greater than that of the elements taken separately."

It is interesting to trace the existence of the compound Fe_2Ni from the melting-point determinations of Guertler and Tammann.§ These authors have indeed observed a sharp upward bend in the melting-point curve near the point corresponding to that composition. For some reason, however, which has escaped me, they have assumed, not the existence of this com-

* F. Hegg, Thesis, Zürich, 1910.

† P. Weiss and G. Foëx, *Arch. des Sc. phys. et nat.* (4), **31**, pp. 4 and 89, January, 1911.

‡ R. Hadfield and B. Hopkinson, *J. Inst. E.E.*, **46**, p. 267, April, 1911.

§ Guertler and Tammann, *Zeitschr. anorg. Chemie*, **45**, p. 205, 1905.

pound, but the existence of $FeNi_2$; this latter corresponds to a minimum which is not well marked and which cannot have this meaning.

The want of additivity in the molecular moments of the ferronickels has ceased to be an exceptional fact, since we have recognised that the same atom frequently assumes, in accordance with the conditions of temperature and chemical combination, the different moments which are all integer multiples of the magneton. We have already stated that at very low temperatures the magnetic moment of the nickel atom amounts to 3 magnetons and that of the iron atom to 11 magnetons. The saturation observed for the alloy Fe_2Ni yields exactly 30 magnetons, that is, 10 per atom.

The knowledge of the Curie constant enables us not only to calculate the molecular moments, but also to ascertain whether the atoms of the molecule are rigidly interconnected or whether they are jointed. I wish here more precisely to define the term "molecule," of which I had been making a somewhat vague use. By molecule I understand the group of atoms which are rigidly connected with one another. When I write Fe_3, *e.g.*, that will say that these three atoms of iron form an unchangeable solid, the orientation of which depends upon two co-ordinates only. When, on the contrary, the atoms are interconnected by articulation, admitting of independent orientation, they are, from the magnetic point of view, different molecules, as if they were altogether free.*

The experiments made on β iron have shown that its molecule is Fe_3, that of γ iron Fe_2, and that of δ iron is probably Fe. In nickel and cobalt the molecule, at temperatures above the Curie point, is composed of a single atom. The Curie constant found for Fe_2Ni, as common limit of the constants for the two series of solid solutions, shows that the molecule Fe_2Ni forms a rigid assemblage and yields for this molecule the value of 30 magnetons, as at very low temperatures.

The Curie constants of the interval Fe–Fe_2Ni vary in a continuous manner, starting from the constant for γ iron; these constants approach those of the solutions of Fe_2 and of Fe_2Ni. A certain number of values, moreover, suggest a continuation of the two different Curie constants of β iron. The irreversible phenomena which characterise the ferronickels rich in iron render the interpretation of the relations difficult, however; further experiments are required and are being conducted.

As to the reversible ferronickels, the linear variation of the Curie constant is distinct, except that the last point, corresponding to pure nickel, is not on the straight line. The scale of the diagram in the neighbourhood of Ni is so small, that it would be impossible to see on it alone if the discrepancy, though it amounts to 25 per cent., can be attributed to experimental errors or not. But the exact figure for pure nickel yields 8 magnetons, while the production of the straight line yields 9 magnetons. When we study pure nickel at higher temperatures we observe, at 500° above the Curie point, a change of state which makes the moment of the atom rise from 8 up to 9 magnetons. In the reversible ferronickels the nickel is in a state which the pure metal only assumes at a much higher temperature. This "repercussion" of the neighbouring atoms on the interior magnetic state of the nickel atom is one of the most curious features of these phenomena.

Nickel-Cobalt (*Fig.* 2).—The magnetism of the alloys of nickel and cobalt has been studied by O. Bloch † by the same method and the same apparatus

* Compare the memoir on the magneton as to the development of the consequences of the kinetic theory.

† O. Bloch, Dissertation, Zürich, 1912; to be published also in *Arch. des Sci. phys. et nat.*

used in the study of the ferronickels. The results are strikingly simple. The alloys form in the whole interval Ni–Co one uninterrupted series of solid solutions.

The measurements of the saturations at low temperatures have only been carried out for alloys containing up to 70 per cent. of cobalt. Above that grade the alloys have the extreme magnetic hardness which had already been observed in pure cobalt and had prevented its saturation. Between 0 and 70 per cent. of cobalt the saturation follows exactly a straight-line law; we can therefore determine the saturation of pure cobalt by an extrapolation which does not introduce more than a small uncertainty. We thus find 8·94 magnetons, that is to say, the whole number 9, considering the precision of the experiments.

The Curie constants likewise vary in a linear ratio throughout the interval. The value for pure nickel leads to 8 magnetons; above the Curie point we find for cobalt 15 magnetons. The surrounding cobalt atoms have not the same repercussion effect on the nickel atom as the iron atoms exert.

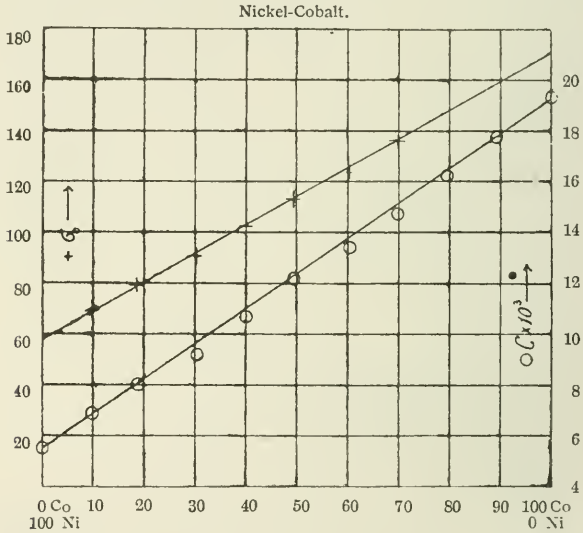


FIG. 2.

Iron-Cobalt.—The results of measurements made on iron-cobalt alloys by A. Preuss* are represented in Fig. 3, which gives the specific saturations at low temperatures and two series of Curie constants, one of which corresponds in its continuity to β iron and the other to γ iron. The three curves are straight lines which are broken at a point corresponding to the compound Fe_2Co, the existence of which is thus established.

As in the case of Fe_2Ni, the specific magnetism of Fe_2Co is greater than it should be if it were a case of mixture. From the magnetism we deduce for Fe_2Co the molecular moment of 36 magnetons, that is to say, 12 magnetons per atom, while iron has only 11 magnetons. Making allowance for the thermal variation between absolute zero and the ordinary temperature and of the ratios of the densities and of the atomic weights of iron and cobalt we see that the saturation intensity of the alloy Fe_2Co is by 10 per cent.

* A. Preuss, Dissertation, Zürich, 1912.

greater than that of pure iron. This result is in contradiction to the current ideas, which seemed to have received a decided confirmation by the already quoted research of R. Hadfield and B. Hopkinson, in which they assert, "that at the present time there is no known iron alloy possessing higher magnetism than pure iron itself." The utilisation of this novel alloy for the construction of pole-pieces for electromagnets is being enquired into.

The straight line which represents the specific saturation between Fe and Fe_2Co shows another peculiarity. It meets the line of pure iron not at the point corresponding to 11 magnetons, as we should expect, but lower down at the value at 10 magnetons. The presence of the molecules of the alloy Fe_2Co thus calls forth a change of state in the atoms of iron. The phenomenon is analogous to what we had observed in the case of the

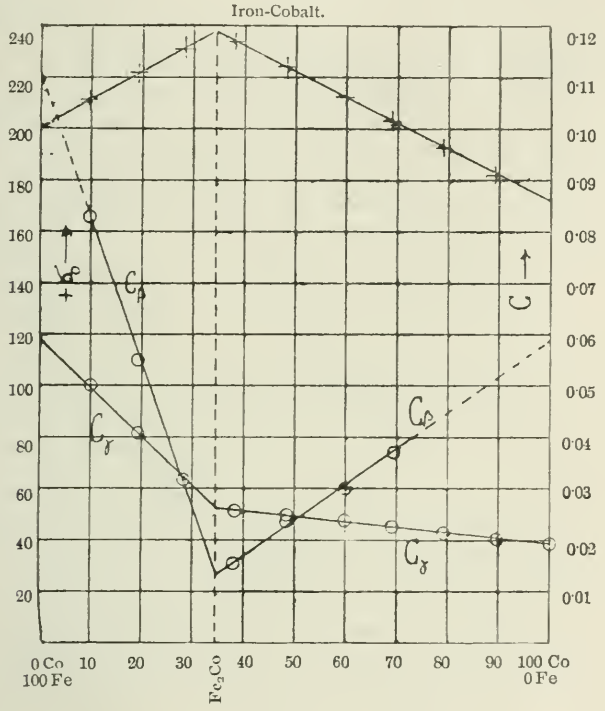


FIG. 3.

reversible ferronickels and pure nickel, with the difference that the change was only produced at high temperatures in this latter case.

The Curie constants yield, as in the previously studied alloys, molecular magnetic moments which are expressed by whole numbers of magnetons. They teach us at the same time which is the molecule of the bodies present in the alloys, the term molecule to be understood in the sense which I defined above. We find that the β iron, the limit of the alloys, is Fe_3 with 20 magnetons per atom, whilst the pure β iron, which is likewise Fe_3, possesses only 10 magnetons per atom. This is a third example of the effect of a repercussion by the surrounding molecules upon the state of the atom. The β iron Fe_3 alloys with the equally rigid molecule Fe_2Co, which differs from it only in so far as one atom of cobalt has been substituted for an atom of

iron. The same alloy Fe_2Co, when alloying with cobalt, obliges the cobalt to treble itself in order to form the rigid molecule Co_3 with 15 magnetons per atom. These alloys of Fe_2Co and Co have, as mentioned, only been found up to 70 per cent. of Co; the probable existence of Co_3 has only been deduced by an extrapolation.

The γ iron is Fe_2; it alloys with Fe_2Co, having 18 magnetons per atom. Its presence, however, forces the ferrocobalt to double itself so as to become $(Fe_2Co)_2$. This double molecule possesses 42 magnetons, *i.e.*, 7 per atom. The other Curie constant of this alloy, corresponding to the simple formula Fe_2Co, also gave 7 magnetons per atom. It is the doubled molecule which intervenes also in the second series of alloys, which represent a continuation of γ iron between the compounds Fe_2Co and Co. Here, however, the cobalt intervenes with a molecule consisting of a unique atom, like the molecule of the metal observed in the pure state. The simple cobalt, Co, and the trebled cobalt, Co_3, have each 15 magnetons per atom.

The principal results of this research are the following:

I have indicated a general method for investigating magnetic alloys formed of a solid homogeneous solution, the experimental results being employed for the determination of the magnetic moments of the molecules and of the atoms.

This method is supplemented and rendered fertile by the theory of the rationality of the ratios between the magnetic moments of the atoms. This theory finds its expression in the statement that there is a common measure for all the magnetic moments of the atoms which has been called the *magneton*. The theory has received numerous confirmations by the study of magnetic alloys.

Once established, the rationality of the ratios between the atomic moments itself serves as a means of investigation. It admits of arriving at new data concerning the molecular edifice when we distinguish the cases in which the atoms are rigidly connected with one another in the molecule from those in which they are free or articulated.

The application of this method to the reversible ferronickels and to the alloys of nickel and cobalt has led to results which do not leave any ambiguity. The study of the irreversible ferronickels is still incomplete. The ferrocobalts are so rich in their diverse phenomena that it would be adventurous to assert that the manner in which the facts have been interpreted is in every respect definitive. This interpretation gives a coherent picture, however, which is suggestive from several points of view, notably with regard to the repercussion effect which the presence of the surrounding molecules has on the interior magnetic state and upon the state of the bondage between the atoms.

The existence and the preponderating influence of the compounds Fe_2Ni and Fe_2Co have been demonstrated. The latter furnishes a metal which, at ordinary temperature, possesses a saturation intensity exceeding that of pure iron by about 10 per cent.

RESEARCHES ON MAGNETISATION AT VERY LOW TEMPERATURES.

Professor Pierre Weiss also communicated the following abstract * of a Paper by himself and **Professor H. Kamerlingh Onnes** on "Researches on Magnetisation at Very Low Temperatures."

The question has often been asked if a gap which cannot be bridged over exists between the ferromagnetic metals of the iron group on the one hand and the paramagnetic metals of the same group on the other, or if the latter metals should also exhibit a very low Curie-point if the temperature were sufficiently lowered.

Ch. Ed. Guillaume † says, with reference to the Heusler alloys of Mn, Al, Cu and Mn, Sn, Cu which are ferromagnetic: "The reason for this can be found in the fact that aluminium or tin, when compounded with manganese, a metal from the magnetic group, raises its transformation temperatures, which, following an hypothesis already suggested by Faraday, ought to lie very low." It can indeed be seen that aluminium and tin raise the melting points of various alloys which they form with other metals (the series Al—Au, Al—Sb, Na—Sn), and seem to possess the general property of raising temperatures of transformation.

We might, therefore, expect that vanadium, chromium, and manganese should at very low temperatures exhibit either the characteristics of ferromagnetism (magnetisation not proportional to strength of field, saturation, hysteresis), or, in conformity with Curie's law, a strongly increased paramagnetism. The susceptibility at the temperature of solid hydrogen should be about twenty times as great as at ordinary temperature.‡ At this time we were not yet aware of the results published by H. du Bois and Honda,§ from which it appears that the inverse proportionality of paramagnetism to the absolute temperature is but one of the possible cases. To get an idea of the order of magnitude of the expected phenomena we may suppose that

* See *Verslagen van de Afdeeling Natuurkunde der Kon. Akad. van Wetenschappen te Amsterdam*, 26 February, 1910.

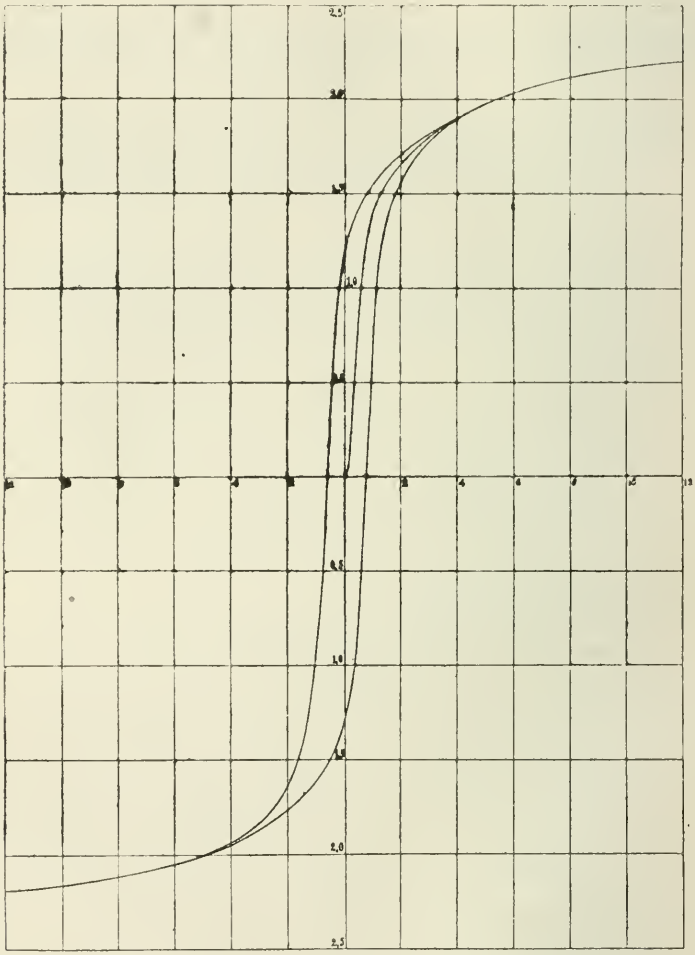
† Ch. Ed. Guillaume, *Actes de la Soc. helv. des Sc. nat.*, vol. i., p. 88, 1907.

‡ A similar supposition formed the starting-point of a research by H. Kamerlingh Onnes and A. Perrier, closely connected with the present subject. This investigation was undertaken at the same time as the present research, and will shortly be published. Using the method of the maximum couple and the hydrostatic rise, the magnetisation of liquid oxygen at various temperatures, and of solid oxygen at the temperatures of boiling and solidifying hydrogen were measured. The increase of the magnetisation at low temperatures was found to be very great, though not so much as was expected, and a distinct deviation from Curie's law and a characteristic curve were found.

§ H. du Bois and Honda, *Proc. Kon. Akad. van Wet.*, January, 1910.

the paramagnetic γ iron still exists at 14° K. (Kelvin degrees) with the same Curie constant (product of absolute temperature by susceptibility). In that case a value of about 400 is found for the magnetisation of this substance in a field of 20,000 gauss.

When we now introduced into our apparatus roughly formed ellipsoids of Moissan vanadium and Goldschmidt chromium and manganese in succession, the awaited change did not appear. In every case the deflection at the temperature of solid hydrogen as well as at that of hydrogen boiling under



atmospheric pressure remained the same as it was at ordinary temperature, that is, to a few tenths of a millimetre, and these must be ascribed to the magnetism of the suspending apparatus. There was therefore no ferromagnetism, and we were obliged to choose between the following two hypotheses for these substances. We were either dealing with paramagnetism of a new kind or with diamagnetism, which is also found in copper, while most of the salts of this metal are paramagnetic. Du Bois and Honda's paper, in which these three metals are classified under those whose para-

magnetism is invariable or increases with the temperature, shows that the first assumption is the correct one. The behaviour of copper made us consider the other hypothesis a reasonable one.

One could always assume that the paramagnetism, which, as a general rule, is ascribed to the metallic manganese, results from the presence of its oxides, which are strongly magnetic, or of a small quantity of iron. To put this assumption to the proof we prepared very pure manganese from Merck's pure chloride, which had been proved free from iron. The preparation was accomplished by electrolysing the salt between a cathode of distilled mercury and an anode of platinum alloyed with 40 per cent. of rhodium, which is not attacked by the chloridion. The amalgam obtained in this way was separated in a stream of pure, dry hydrogen. In this way a grey powder was obtained which, when compressed in a glass tube as a mould, took the shape of a solid rod. A rod prepared in this manner exhibited paramagnetism. A glass tube with the powdered manganese was also paramagnetic. The same manganese contained in a magnesia boat was thereupon fused in an electric-resistance furnace, and in an atmosphere of hydrogen. In this way an ingot was obtained which was covered with a light oxidised crust. It was found impossible to grind away this crust with quartz powder, since the metal was of the same hardness as quartz. Emery could not be used as it is magnetic. The impure crust was therefore turned off with a diamond tool, and a small cylinder of pure substance was obtained.

This cylinder was found to be ferromagnetic. The accompanying figure gives the hysteresis curve for this substance. The maximum value of the specific magnetisation is 100 times weaker than that of iron, and the coercive field is 670 gauss, that is to say, 10 times as strong as the coercive field of steel which is used for the preparation of good permanent magnets. This peculiar substance seems moreover to have striking magneto-crystalline properties. The rod was strongly attracted between the poles of a magnet and placed itself perpendicular to the field.

Manganese of the same degree of purity can therefore occur in two states : paramagnetic and ferromagnetic.

As regards the ferromagnetism of manganese, this had already been observed by Seckelson* with electrolytic manganese that was liberated at 100° C. from the chloride upon a platinum wire, and with a regulus prepared by Bunsen from manganese fluoride. The very indefinite observations concerning the magnetisation which he published do not contradict with our measurements.

* Seckelson, *Wied. Ann.*, lxvii., p. 37, 1899.

THE MAGNETIC PROPERTIES OF COMPOUNDS IN RELATION TO THEIR STOICHIOMETRIC COMPOSITION.

Professor E. Wedekind (Strassburg) read a Paper on "The Magnetic Properties of Compounds in Relation to their Stoichiometric Composition."

In order to give an account of the magnetic properties of certain alloys, with a view to establishing their connection with the chemical relationships, it is necessary first of all to know which components are indispensable for exhibiting magnetic properties in alloys hitherto investigated. Passing by iron, nickel and cobalt, which have long been known to possess magnetic properties both in alloys and in compounds, we come to the more recent investigations of manganese, chromium, and, in a certain degree, vanadium also. These metals themselves are but feebly paramagnetic, but are able to form alloys or compounds which are more or less magnetic; these elements may be described as possessing "latent magnetism."

As is well known, the work of Tammann* and Honda† has shed much light on the magnetisability of the alloys of *ferromagnetic* metals. In almost all cases the binary compounds of these with other metals are not appreciably magnetisable, in contrast with the mixed crystals which the ferro-magnetic metals as solvents form with the other metals. On the other hand, the mixed crystals, which are to be considered as solutions of ferromagnetic metals in non-magnetisable metals, are not magnetic; which, indeed, is the case if ferromagnetic crystals are dissolved in them (there are, for example, non-magnetic nickel-cobalt alloys). The ferromagnetism of alloys is in relation to its dependence on the concentration determined by its being associated with a special form of crystal. Moreover, the influence of chemical compounds present prevails, and these may suppress or entirely destroy the ferromagnetism of the principal components.

From this one may conclude that well-defined chemical compounds of ferromagnetic metals possess for the respective molecules peculiar magnetisability. This applies not only to compounds with other metals, whose characterisation is usually possible only by metallographic means, but also to compounds of the non-metals (carbon, oxygen, nitrogen, boron, &c.). For example, the vast difference in the magnetic properties of iron and of its oxide, Fe_2O_3, is well known. However, at the same time, in the series of iron oxides there is some disagreement with this rule, as exemplified by the existence of the strongly magnetic oxide Fe_3O_4, which occurs in nature as the lodestone. Recently, S. Hilpert‡ has explained these relationships by his investigations of the compounds of iron oxide with bivalent bases, the so-called *ferrites*, of the general formula $MO \cdot Fe_2O_3$.

The potassium, sodium, calcium, barium, magnesium, zinc and lead ferrites

* *Zeitsch. f. physik. Chemie*, 65, 73, 1909.
† *Annal. d. Physik.*, 32, 1005, 1910.
‡ *Berichte d. deutsch. chem. Ges.*, 42, 2248, 1909.

are not magnetic and do not become so until they are strongly heated. The compounds of copper, cobalt, and ferrous oxides with ferric oxide are far more strongly magnetic, and indeed they separate out of solution directly in the magnetic state; these precipitates are almost black in contrast with the non-magnetic precipitates, which are light red. All ferrites show the same peculiarity as iron does: that is to say, on exceeding a certain temperature they become non-magnetic, from which it follows that the compounds of iron oxide always form magnetic modifications when it functions in them as an acid. The permeability of copper ferrite is of the same order of magnitude as with the lodestone; the transition point is about 280°. Cobalt ferrite loses its magnetism completely at 280° to 290°, and regains its former strength again on cooling. Finally, a peculiar complex is produced by the union of lead oxide, copper oxide, and iron oxide; it is stable only at higher temperatures: on slowly cooling, the strongly magnetic mass loses its magnetisability. By repeated heating to 900°, followed by rapid cooling, the original condition can be easily reproduced; on melting (*ca.* 1,300°) the permeability disappears once more. This is very considerable (about half as great as that of metallic iron; also the fact is worthy of notice from the technical standpoint, that this lead-copper ferrite is almost an electrical insulator, its electric resistance being about 10^{10} times greater than that of iron. Thus we have here a substance which conducts badly but possesses strong temporary magnetism; it should therefore be of much service in electrotechnics.

There can therefore be no doubt that the strong magnetisability of ferrosoferric oxide, $FeO . Fe_2O_3$, depends upon the acid function of the iron oxide, or on the combination of the two components; in this connection special attention should be called to the fact that ferrous oxide exhibits no ferromagnetic properties. Also very interesting, appearing at first to be in contradiction to these descriptions, is the existence of a magnetic ferric oxide. It has, however, been proved to be a ferric ferrite, $Fe_2O_3 . 2Fe_2O_3$, which on strong heating passes into ordinary ferric oxide, at the same time losing its magnetisability. Cobaltic ferrite, $Co_2O_3 . 2Fe_2O_3$, is an analogous compound of similar properties. In any case, the formation of the two compounds, ferrous ferrite and cobaltous ferrite, follows from the oxidation of a part of the molecule which does not come into consideration as carrier of the magnetic properties.

Of other compounds of iron it is known that they are essentially more feebly magnetic than the metal; but it is to be anticipated that later on some relationship between their magnetic properties and their chemical constitution will be discovered here also. But mention may be made of the notable fact that there are also diamagnetic compounds of the ferromagnetic metals, *e.g.*, the iron and nickel carbonyls; potassium ferrocyanide belongs here, as also do most of the cobaltamine (luteo-, purpureo-, praseo-) salts.

If one now extends these considerations on the changes of magnetic properties of the metals occurring on their passage into simple binary compounds to those metals which *precede* iron in the periodic system of the elements, thus first of all to manganese and chromium, one finds here the reverse relationship in so far as these, in themselves not ferromagnetic elements, are able to form with certain metalloids comparatively strongly magnetic compounds; while on the other hand the ferromagnetic metals, especially on addition of manganese, lose more or less of their magnetic power. The ferromagnetic alloys of Heusler are well known, particularly the manganese-aluminium bronzes, which possess the peculiarity that they do not attain the maximum of magnetisability until they have undergone

an artificial ageing—that is, by several hours' warming at 110–130° (the magnetisability amounts to about two-thirds that of cast iron). In this connection it was early recognised that magnetic properties are associated with the stoichiometric composition of manganese compounds, and that definite chemical combinations are the carriers of ferromagnetism. According to Heusler and Richarz,* in the alloys prepared from 30 per cent. manganese-copper and aluminium the magnetic molecule ought to contain aluminium in chemical combination with manganese and copper atoms; and, indeed, so that three atoms of the other metals are bound to one atom of aluminium, corresponding with the formula $Al_x(Cu,Mn)_{3x}$.

The first definite *compounds* of manganese which were magneto-chemically investigated were the *borides*,† when it appeared that it was not so much the nature of the two components which decided the magnetic properties as the stoichiometric composition. Boron and manganese form two well-defined compounds, corresponding with the formulæ MnB and MnB_2, of which the monoboride, MnB, is strongly ferromagnetic and is to be considered as the actual carrier of the magnetism in the manganese-boron melt, while the diboride, MnB_2, has no marked ferromagnetic properties. Amongst the manganese-boron melts, that containing 12 per cent. boron showed the highest permeability, although the ferromagnetic monoboride contains 16·6 per cent. This contradiction is to be referred to the presence of small quantities of MnB_2 in the MnB, which depress the magnetism to a marked degree. Corresponding with the borides are two compounds of manganese with antimony, MnSb and Mn_2Sb, also a phosphide, arsenide, bismuthide and others. The quantitative comparison of the compounds first named showed that the antimonide MnSb has the highest permeability; the boride MnB comes next, but is considerably inferior, then the antimonide Mn_2Sb; still more feebly magnetic is the phosphide. A comparison with cast iron shows that this is about 10·5 times as strong as the antimonide MnSb. This comparison is displayed in the accompanying curve (see next page).

Some of these manganese compounds show the magnetic peculiarities of *steel;* that is, they are capable of permanent magnetism, and so possess residual magnetism and coercive force; and, indeed, those compounds which are relatively weak and temporarily magnetic (MnB and Mn_2Sb) retain their poles according to their magnetisation, and have coercive forces which are not only significantly greater than those in the magnetic kinds of soft iron, but surpass, in this respect, even cast iron and wolfram magnet steel. The boride possesses the greatest coercive force (33·4); then follow Mn_2Sb with 30·9, and MnSb with 8·2. The phosphide exhibits no measurable coercive force. Here we have then a property in which certain manganese compounds excel iron. True, the permanent magnetisation is always less than that of steel, but in the boride it is nevertheless considerable. Ordinary steel is only something like twice as strongly permanently magnetic as manganese boride, out of which magnetic needles can be made. The permanent magnetism of the antimonide MnSb is about half as great as that of the boride MnB, but still always greater than the residual magnetism of soft iron. The polarity of the boride can be diminished by warming, and it disappears completely at 450°: after renewed magnetisation a slight increase in the residual magnetism takes place, which then gradually goes back again to the former value. The residual magnetism of the phosphide is about 10 times as small as that of the boride. The man-

* *Zeitschr. f. anorg. Chemie*, **61**, 265, 1909.

† Binet du Jassoneix, *Bull. Soc. chim.*, **3**, 35, 102, 1906 E. Wedekind, *Ber. d. deutsch. chem. Ges.*, **38**, 1228; **40**, 1260.

ganese-tin alloys* show a relatively high residual magnetism ; starting with an alloy containing 92 per cent. Mn, it rises fairly regularly with increase of tin, and attains at the concentration agreeing with the formula Mn_4Sn a very well defined maximum, and disappears as the compound Mn_2Sn is approached.

The pure arsenide, MnAs, is also somewhat strongly magnetic,† while the arsenide, Mn_3As_2, manifests an essentially smaller permeability. It is very noteworthy that it is those compounds of manganese with *diamagnetic* elements (boron, antimony, arsenic) which are so pronouncedly magnetic. It

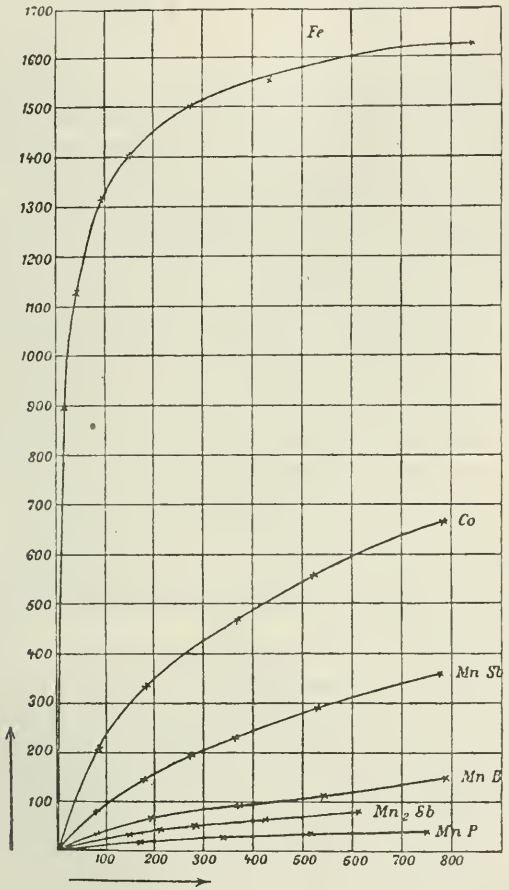


FIG. 1.

is therefore not surprising that the most strongly diamagnetic element, bismuth, likewise forms a fairly strongly magnetisable compound, the bismuthide, MnBi.‡ It is remarkable that even a small proportion of manganese suffices to obtain a distinctly magnetic bismuth metal ; bismuth, also antimony, containing only $\frac{1}{4}$ per cent. of manganese, is attracted by a powerful horseshoe magnet. Some manganese compounds are distinguished by comparatively

* Honda, *Annal. d. Physik*, 4, 32, 1025, 1910.
† S. Hilpert and Dieckmann, *Ber. d. deutsch. chem. Ges.*, 44, 2669, 1911.
‡ E. Wedekind and Th. Veit, *Berichte d. deutsch. chem. Ges.*, 44, 2665, 1911.

low transition points ;* for instance, the phosphide becomes non-magnetic even at summer temperature, but it can be rendered magnetic again by immersion in cold water. The magnetic transition points of compounds with elements of the fifth group of the periodic system arrange themselves, according to Hilpert and Dieckmann, in the same sequence as the atomic weights of the elements which are united to the manganese, as is seen in the following table :—

MnP	...	...	18–26°
MnAs	...	...	40–45°
MnSb	...	...	320–330°
MnBi	...	...	360–380°

Gaseous elements are also able to produce magnetic compounds with manganese. The manganese oxides will be considered later ; but here reference need be made to the *nitrides* † only. The magnetisability of the manganese-nitrogen combinations increases with rise in the manganese content, as observed with the nitrides, Mn_3N_2, Mn_5N_2, Mn_7N_2. The last is relatively strongly magnetic, and also exhibits residual magnetism.

These facts suffice for it to be recognised that the magnetism of compounds is a decided *molecular* property. It may be seen among manganese compounds that the nature of the two components works quite definitely on the appearance of the "latent" magnetism of the manganese ; but that the stoichiometric composition is determinative is to be seen, for example, from the observations on the manganese-boron systems. Melts of the two components are magnetic only in consequence of the presence of the actual carrier of this property, the monoboride, MnB ; while the diboride, MnB_2, present at the same time, is not ferromagnetic. Once more may be recalled the great differences observed in the permeability of the antimonides, MnSb and Mn_2Sb, as well as of the arsenides, MnAs and Mn_3As_2. It is to be observed in this connection that the two *iron* arsenides are entirely non-magnetic, whence it appears to follow that this component (arsenic) can exercise with a ferromagnetic and with a latent magnetic metal entirely opposite influences.‡

Although, then, there can be no doubt about the existence of relationships between magnetisability and stoichiometric composition, it still remains to ascertain the degree of *valency* of those polyvalent metals, which attains with manganese the *maximum* of magnetic properties. If one surveys now the magnetic manganese compounds hitherto mentioned, it appears that, with one exception (manganese-tin), they contain typically *tri*valent elements ; boron, nitrogen, phosphorus, arsenic, antimony and bismuth. Apart from the nitrogen compounds, it is found that the maximum of magnetisability in each series is attained when the ratio of the components is 1 : 1 ; *e.g.*, in the compounds MnB, MnAs, MnSb.

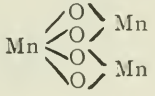
Manganese in these simple binary compounds is thus *tri*valent, and so one must conclude that this element in the trivalent condition develops the maximum of its latent magnetisability. These views find a certain confirmation in the fact that the compounds of manganese with *bi*valent non-metallic elements (sulphide, selenide, telluride, &c.) hitherto investigated are considerably more feebly magnetic § than those compounds with trivalent elements mentioned

* Hilpert and Dieckmann, *loc. cit.*, 2831.
† Wedekind and Veit, *loc. cit.*, **41**, 3769, 1908.
‡ Hilpert and Dieckmann, *loc. cit.*
§ Wedekind and Veit, *loc. cit.*, **44**, 203, 1911.

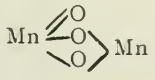
above; so also those with quadrivalent elements, as manganese-tin, Mn_4Sn, while the silicide, Mn_2Si, is scarcely magnetic (in this substance the manganese may be bivalent).

If one examines more closely the relation between the magnetisability and the valency of a strongly paramagnetic element with several degrees of valency, then the second component must be so chosen that it forms, as far as possible, well defined compounds of all the valencies belonging to the given metal. It is not easy to fulfil this requirement, but an approach is made when the second component is oxygen or sulphur, which often provides several forms of compound. The following compounds of manganese are applicable to such an investigation: MnO, Mn_2O_3, Mn_3O_4 and MnO_2. The oxide of hexavalent manganese is not known in the pure state, and the properties of the heptoxide do not permit of close examination. To this must be added that the oxide Mn_3O_4 represents no independent degree of oxidation (which holds good also for the oxide Mn_2O_3, although it might be the sesquioxide of trivalent manganese).

Comparative measurements by means of the magnetic balance have now shown* that, of the four manganese oxides, that having the composition Mn_3O_4 is the most strongly magnetic; of the two independent oxides the lower oxide, MnO, is more magnetic than the dioxide, MnO_2. The sesquioxide Mn_2O_3 behaves similarly to the oxide Mn_3O_4. Thus we find here the same phenomenon as with iron; the "mixed" oxide Mn_3O_4 is the most strongly magnetisable (the susceptibility as such is naturally much smaller than it is with the lodestone). Here the salt-like character of the oxide becomes evident without further comment, as Mn_3O_4 has been viewed for some time from the chemical standpoint as the manganous salt of orthomanganous acid—



and now the formula of the sesquioxide as a manganous salt of metamanganous acid—



receives support on magnetochemical grounds.

Naturally, in this particular case, not much has been gained from the formulation of the question, as only two independent oxides could be submitted to investigation.

Much better prospects were offered by a comparative examination of the oxides of *vanadium*, of which there are four. From the periodic system of the elements it may be foreseen that vanadium, followed by chromium and manganese, likewise possesses latent magnetism, although to a smaller degree. This assumption has been confirmed;† while the metal is only feebly paramagnetic ($\chi = 3{\cdot}8 \times 10^{-6}$) the sub-oxide, VO, proves to be more strongly magnetic than manganese dioxide or chromium oxide, and about half as strongly magnetic as iron oxide. A comparison of the four oxides of vanadium, VO, V_2O_3, VO_2, V_2O_5, showed that the susceptibility falls off with increase of oxygen content; *i.e.*, with the valency. Hence, arranged in the

* Unpublished experiments by E. Wedekind and C. Horst.

† Wedekind and Horst, *Berichte d. deutsch. chem. Ges.*, **45**, 262, 1912.

ascending order of their susceptibility, they form the series V_2O_5, VO_2, V_2O_3, VO. The pentoxide is only very feebly paramagnetic ($\chi = 0{\cdot}86 \times 10^{-6}$).

As vanadium forms also a series of *sulphides*, opportunity was afforded to study the relation between susceptibility and valency by means of another element. Unfortunately the experiments with sulphur failed with regard to the disulphide, VS_2, corresponding with the dioxide, as the product proved to be the oxysulphide, VOS. The differences in susceptibility of the vanadium sulphides are by no means so great as in the series of oxides. But it is very remarkable that the sequence of the sulphides according to their magnetisability is directly opposed to that of the oxides. In the order of their susceptibility the vanadium sulphides arrange themselves as follows :—

$$VS,\ V_2S_3,\ V_2S_5.$$

It follows from this that the second component may be of determining influence on the susceptibility of such simple compounds of the paramagnetic

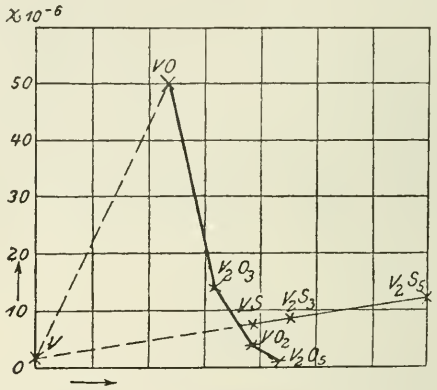


Fig. 2.

metals. In this case it is natural to take into consideration that oxygen is relatively strongly paramagnetic, while sulphur belongs to the diamagnetic elements.

The observed relationship between the specific susceptibility and stoichiometric composition is displayed very clearly in the accompanying graph, in which the susceptibilities of the oxides and sulphides of vanadium are plotted as ordinates and the percentage of oxygen and sulphur as abscissæ. It is particularly remarkable that the sulphides fall along a straight line, while each oxide falls at a kink in a curve.

It may be mentioned that vanadium oxysulphide, VOS, has proved to be substantially more strongly magnetic than the nitride. As vanadium in both compounds is trivalent, one may recognise here the determining influence of the second components.

In the case of vanadium, there can be no doubt as to the dependence of the magnetising number on the valency. It still remains to prove this relation with compounds of other latent-magnetic metals. Unfortunately, nowhere are the conditions so favourable as with vanadium.

Next to manganese must *chromium* be considered.

Chromium metal itself is only a little more strongly magnetic than manganese metal, but for more than fifty years have we known, from the

observations of Fr. Wöhler,* that there is a ferromagnetic oxide, Cr_5O_9, which is formed by heating chromylchloride. Recently there has been added a far more strongly magnetisable oxide, Cr_4O_9.† Many other simple chromium compounds (boride, nitride, &c.) have a somewhat higher susceptibility than the metal. Chromium may be bi-, tri-, quadri-, and hexa-valent; but there are only two independent oxides, Cr_2O_3, and CrO_3, which are available for measurements, as the oxides CrO and CrO_2 are scarcely known in the pure state. Pentavalent chromium is known only in the form of organic derivatives.

A comparison of the sesqui- and tri-oxides of chromium has now shown‡ that the latter is scarcely magnetisable, while the sesquioxide has about half the susceptibility of vanadium monoxide. Pentavalent chromium, so far as it can be compared at all, occupies a middle position. The same regularity is found here as with manganese and vanadium; the susceptibility in the series of oxides decreases with rise in the oxygen content, *i.e.*, with the valency of the metal. Further, we have here a satisfactory agreement with the results obtained with iron and manganese, in so far as the mixed oxides are much more strongly magnetisable than the oxides which correspond with a definite degree of valency; also here the saline nature of these compounds, or the acid function of the chromium trioxide, can be made accountable for the rise in the magnetic number, for the magnetic oxide Cr_5O_9 may be expressed as $2(Cr_2O_3) . CrO_3$ and the oxide Cr_4O_9 as $Cr_2O_3 . 2(CrO_3)$. Again, it is found to hold equally good among the chromium sulphides, of which three are known: CrS, Cr_2S_3, and Cr_3S_4. The last again has the highest susceptibility, as a double compound of mono- and sesqui-sulphides, but pure CrS is itself more magnetic than the sesquisulphide, Cr_2S_3.

Of the two independent oxides of manganese, the one poorer in oxygen (MnO) is more magnetic than the dioxide (MnO_2), as already stated. Unfortunately, only one synthetic manganese sulphide is known so far (there occurs in nature a disulphide isomorphous with pyrites), so that here it is not possible to make a comparison.

A peculiar case is exhibited by *copper*, which itself is feebly diamagnetic, but in many cupr*ic* compounds is strongly paramagnetic, while most cupr*ous* compounds are diamagnetic.

In conclusion, the results of the investigations here described may be summarised in the following statements:—

1. The magnetisability of simple chemical compounds, which are derived from a ferromagnetic or a latent-magnetic metal, is a well-defined molecular property, which is associated with the stoichiometric composition or constitution of the compound.

2. Simple compounds of ferromagnetic metals are throughout essentially more feebly magnetic than are the metals themselves, so far as they represent one particular degree of valency.

3. Simple compounds of the latent-magnetic metals (Mn,Cr,V, and probably also Ti) are generally more strongly magnetic than the metals; the maximal magnetisability is, nevertheless, determined by the stoichiometric composition, especially where several compounds of the same components exist. Manganese has a maximum in the trivalent condition when combined with such elements as can themselves be trivalent, *i.e.*, when the atomic ratio is 1 : 1. Some of these compounds act as permanent magnets.

* *Annal. d. Chemie*, **111**, 117, 1859; compare A. Genther, *loc. cit.*, **118**, 62, 1861.
† J. Shukow, *Compt. Rend.*, **146**, 1396, 1908.
‡ By unpublished experiments of Wedekind and Horst.

4. With the independent oxides of manganese, chromium, and vanadium, the susceptibility appears as a function of the metal content; with the sulphides of vanadium as a linear function of the sulphur content; it is thus dependent on the valency of the metal in the respective compound.

5. So-called mixed oxides or sulphides, which represent no single degree of valency, are for the *total* metals more strongly magnetic than the independent forms of compound; this is connected with the *acid* nature of one of the components, which always exhibits the higher degree of valency. Such a compound always reveals itself when graphically represented by a sharp break in the curve.

6. The magnetisability generally falls off with a lowering of the atomic weight of the principal metal; several manganese compounds are ferromagnetic; of chromium, only the two above-mentioned mixed oxides. No vanadium compound is decidedly ferromagnetic. To the left of vanadium stands titanium and its compounds, the investigation of which is now in hand, and with this element the minimum will be reached, as scandium, which comes next in the same direction, as oxide, is diamagnetic.

Lastly, attention may be called to another interesting group of magnetic compounds, namely, to some of the *rare earths*, of which the oxides of neodymium, europium, gadolinium, terbium, and dysprosium, show extraordinarily high magnetic values, which may serve for the characterisation of the respective earths. Here there is scarcely any connection with valency, but on the other hand there appears a periodic dependence on the atomic weight, which later on will no doubt permit the drawing of a susceptibility-atomic weight curve in the group of the rare earths.

I will not close without expressing the conviction that the relationships hitherto found between magnetic properties and chemical nature are not of interest on purely magnetochemical considerations alone; but that they have also the prospect of becoming a practical means of help to the investigation of molecular structure, as has been already exemplified in the case of manganese sesquioxide.

THE NATURE OF THE HEUSLER ALLOYS.

A Paper on "The Nature of the Heusler Alloys" was communicated by **Dr. Fr. Heusler** (Director of the Isabellenhütte Ltd., Dillenburg) and **Dr. E. Take** (Lecturer on Physics at the University of Marburg).

The ferromagnetic manganese alloys were discovered by F. Heusler in 1898, and named after him. They contain in addition to manganese, or manganese-copper, *one* more element, viz., aluminium, tin, arsenic, antimony, bismuth or boron. Of these various alloys the aluminium-manganese bronzes show by far the strongest ferromagnetism ; they have most fully been investigated for this reason, and the following considerations are, in the first instance, to be limited to this group of alloys.

Part I.

THE PROPERTIES OF ALUMINIUM-MANGANESE BRONZES.

By Dr. E. Take.

We owe our first exact information concerning the aluminium-manganese and copper alloys to the investigations which F. Heusler* conducted in the chemical laboratory of the Isabellenhütte at Dillenburg, and further to the magnetometric determinations by W. Starck and E. Haupt.† The latter two researches were carried out on the direct instigation of Heusler, and under the co-operation of F. Richarz, in the Physical Institute of the University of Marburg, where they were later on continued by E. Take,‡ Asteroth,§ Preusser,‖ Dippel,¶ and F. A. Schulze.**

* Fr. Heusler, "Ueber magnetische Manganlegierungen," *Verhandl. Deutsch. Physik. Ges.*, **5**, p. 219, 1903 ; deposited in the archives of the Society on June 18, 1901.

† F. Heusler, W. Starck and E. Haupt, "Magnetisch-chemische Studien," *ibid.*, **5**, pp. 219-232, June 12, 1903. Complete memoir in the *Schriften d. Ges. zur Beförderung d. gesamten Naturwissenschaften zu Marburg*, Part. V., **13**, pp. 237–300, 1904 : *Ueber die ferromagnetischen Eigenschaften von Legierungen unmagnetischer Metalle*, by F. Heusler and—with the co-operation of F. Richarz—by W. Starck and E. Haupt, reprinted and published as pamphlet by N. G. Elwert, Marburg (price 3.20 marks). The experimental part of the memoir was fully described in the inaugural dissertation of E. Haupt, Marburg, 1904. See further a later *résume* by F. Heusler, "Magnetische Manganlegierungen," *Wallach-Festschrift*, pp. 467–477, Göttingen, 1909 : Vandenhoeck and Ruprecht.

‡ E. Take, "Magnetische und dilatometrische Untersuchungen der Umwandlungen Heuslerscher ferromagnetisierbarer Manganlegierungen," *Schriften Ges. Beförderg. gesamt. Naturw. zu Marburg*, Part VI., **13**, pp. 299–404, 1906 (published also in pamphlet form by N. G. Elwert, Marburg, price 4.00 marks). Preliminary communication in *Ges. Beförderg. Naturw., Marburg*, August 13, 1904 (*Sitzungsberichte*, 1905, pp. 35-49), and in the meeting of the Deutsch. Physik. Ges., March 3, 1905 (*Verhandl.*, **7**, pp. 133–145, 1905). E. Take, "Alterungs- und Umwandlungsstudien an Heuslerschen ferromagnetisierbaren Aluminium-Manganbronzen, insbesondere an Schmiedeproben," *Abhandlg. Kgl. Ges. Wissensch.*

Notes continued on next page.

The investigation of these highly interesting alloys had meanwhile been taken up also in other institutions, and the observations made were confirmed—partly without acknowledgment or with insufficient acknowledgment of this priority and further extended by Austin,*¶ Gumlich,† Hill,‡ Fleming,§ Hadfield,§ A. Gray,‖ Guthe,¶ McLennan,** Ross,†† Zahn and H. Schmidt,‡‡ J. G. Gray,§§ R. E. Gray,‖‖ Knowlton,¶¶ Clifford,*** Stephenson,††† Tokmatshew,‡‡‡ and Steiner.§§§

* L. Austin, "Beobachtungen über die Magnetische Längenänderung der Heuslerschen Legierungen," *Verh. Deutsch. Physik. Ges.*, **6**, pp. 211–216, 1904.

† E. Gumlich, "Versuche mit Heuslerschen Legierungen," *Annal. Physik.* (4), **16**, pp. 535–550, 1905.

‡ Bruce V. Hill, "Note on the Irreversibility of the Heusler Alloys," *Phys. Rev.*, **21**, pp. 335–342, 1905 (Note by E. Take, *Marburg Ges.*, 1906, p. 304, *loc. cit.*); *Phys. Rev.*, **23**, pp. 488–503, 1906.

§ J. A. Fleming and R. A. Hadfield, "On the Magnetic Qualities of some Alloys not containing Iron," *Royal Soc. Proc.*, A, **76**, pp. 271–283, 1905 (Note by Heusler, *Marburger Sitz. Ber.*, 1905, pp. 98–99).

‖ Andrew A. Gray, "Note on Heusler's Magnetic Alloys of Manganese, Aluminium, and Copper," *Roy. Soc. Proc.*, A, **77**, pp. 256–259 (Note by E. Take, *Marburg Ges., loc. cit.*, p. 402, 1906).

¶ K. E. Guthe and L. W. Austin, "Experiments on the Heusler Magnetic Alloys," *Bull. Bureau Standards*, **2**, pp. 297–316, 1906.

** J. C. McLennan, "On the Magnetic Properties of Heusler's Alloys," *Phys. Rev.*, **24**, pp. 248–249, 1907.

†† Alexander D. Ross, "Heusler's Magnetic Alloys," *Roy. Soc. Edinb. Proc.*, **27**, pp. 88–92, 1907. *Magnetic Alloys formed from Non-Magnetic Materials*, Inst. of Metals, Glasgow, September, 1910; *Nature*, **84**, p. 421, 1910; *Journ. de Phys.* (5), **1**, pp. 117–123, 1911.

‡‡ Zahn and H. Schmidt, "Ueber Halleffekt und verwandte Erscheinungen bei einigen Heuslerschen Legierungen," *Verh. Deutsch. Physik. Ges.*, **9**, pp. 98–108, 1910.

§§ James G. Gray, "Experiments with Heusler's Magnetic Alloys," *Roy. Soc. Edinb. Proc.*, **28**, pp. 403–412, 1908.

‖‖ A. D. Ross and Robert E. Gray, "On the Magnetic Properties of certain Copper Alloys," *Roy. Soc. Edinb.*, **29**, pp. 274–286, 1909. *Zeitschr. anorgan. Chemie*, **63**, pp. 349–352, 1909 (Note by Heusler and Richarz, *ibid.*, **65**, pp. 110–112, 1910).

¶¶ A. A. Knowlton, "Preparation and Properties of the Heusler Alloys," *Phys. Rev.*, **30**, pp. 123–125, 1910, and **32**, pp. 54–68, 1911.

*** A. A. Knowlton and C. C. Clifford, "Magnetic Properties of the Heusler Alloys," *Phys. Rev.*, **30**, pp. 125–126, 1910.

††† E. B. Stephenson, same subject, *Phys. Rev.*, **30**, p. 127, 1910, and **31**, pp. 252–260, 1910.

‡‡‡ S. Tokmatshew, "Das Kerrsche Phänomen im Magnetfelde und die Heuslerschen Legierungen," *Journ. Russian Phys. Chem. Soc.* (Phys. Part), **42**, pp. 15–30 and 353–354, 1910.

§§§ Desider Steiner, "Die Hysteresisverluste der ferromagnetisierbaren Mangan-Aluminium Bronzen in Abhängigkeit von der Frequenz des Wechselfeldes," *Annal. Physik.* (4), **35**, pp. 727–754, 1910.

Notes from page 169 continued.

Göttingen, Math.-Physik. Kl., Neue Folge, **8**, No. 2, 1911 (Berlin, 1911 : Weidmann, price 8 M.).

§ P. Asteroth, *Einfluss der thermischen und mechanischen Vorgeschichte auf die magnetischen Eigenschaften, insbesondere die Hysterese Heuslerscher Legierungen*, Dissertation, Marburg, 1907; also *Verh. Deutsch. Physik. Ges.*, **10**, pp. 21–32, 1908; preliminary communication by F. Heusler, *Sitz. Ber. Ges. Beförd. Naturw. Marburg*, November, 1905, p. 98.

‖ W. Preusser, *Ueber die Abhängigkeit der magnetischen Eigenschaften Heuslerscher Aluminium-Manganlegierungen von ihrer chemischen Zusammensetzung*, Dissertation, Marburg, 1908, preliminary communication by F. Heusler, *Sitz. Ber. Marburg*, 1908, p. 203; also F. Heusler and F. Richarz, "Studien über magnetisierbare Manganlegierungen; über Mangan-Aluminium-Kupfer," *Zeitschr. anorgan. Chemie*, **61**, pp. 265–279, 1909.

¶ E. Dippel, *Abhängigkeit der spezifischen Wärme gewisser Legierungen von der thermischen Vorgeschichte und ihr Zusammenhang mit den magnetischen Eigenschaften bei Heuslerschen Legierungen*, Inaugural Dissertation, Marburg, 1910.

** F. A. Schultze, *Leitfähigkeit und thermoelektrische Kraft Heuslerscher Legierungen*, *Verhandl. Deutsch. Physik. Ges.*, **12**, pp. 822–823, 1910.

It would lead too far to reproduce all the observations recorded up to the present even in short abstracts. They shall be referred to only in so far as is rigorously necessary for a clear understanding of the subject and for an easy and convenient orientation.

In spite of the extremely low magnetic susceptibility of their constituents some of these alloys display a very high susceptibility; the highest saturation observed is about a third of that of magnetically very soft iron.

Of the three components, aluminium, manganese, and copper, aluminium * and copper † are doubtlessly paramagnetic and possess a constant susceptibility of $+ 1{\cdot}88 . 10^{-6}$ and $-0{\cdot}82 . 10^{-6}$. As regards the susceptibility of manganese, authorities differ somewhat. Honda ‡ found paramagnetism in this metal as well, but he remarked that the metal appeared to be unsteady. The latter would also follow from the work of P. Weiss, § who observed in the same sample of chemically pure manganese paramagnetism or ferro magnetism, according as the material was in the powdered state or was fused to a massive lump in a current of hydrogen. Ferromagnetism had moreover already been noticed in manganese by Seckelson; || his statements on the magnetisation of his specimens do not appear very definite, however.¶ A very comprehensive enquiry into the magnetisation of manganese has quite recently been made by Ihde.** He found in all his specimens ferromagnetism with regard to the inconstancy of the susceptibility, since the values always increased to a well-defined maximum, to decrease again afterwards. *Qualitatively*, therefore, manganese would decidedly have to be considered as ferromagnetic. When we regard the susceptibilities measured by Ihde from the purely quantitative standpoint, on the other hand, we recognise that manganese differs to a relatively slight extent only from the paramagnetic substances; for the highest values of the susceptibility found were of the order of $100 . 10^{-6}$—which is still 10^{4}–10^{5} times smaller than the susceptibility of the Heusler aluminium-manganese bronzes.

It is true that most of the Heusler alloys contain, in addition to the three elements mentioned, some minimal impurities. Heusler's own specimens were produced by him by melting aluminium together with commercial manganese-copper (30 per cent. of Mn); they contain, as a result, even traces of iron (about 0·4 per cent. on average). In order to investigate the influence of the presence of iron, some manganese-copper of high iron percentage was selected for experiments; †† but it was found impossible to determine the presence of even 1·2 per cent. of iron in manganese-copper by magnetometrical means.

It is, moreover, known also from the researches of Honda ‡‡ that so small a percentage of iron as occurs in the Heusler specimens does not call forth ferromagnetism with respect to the order of the magnetic intensity. Honda states as to this point (p. 1037): "When the iron has formed, with the chief metallic constituent, a compound or some mixed crystals which are poor in

* Compare A. B. Wills, *Phys. Rev.*, **6**, p. 223, 1898, and *Phil. Mag.* (5), **45**, p. 432, 1898; and further the somewhat different values of the susceptibilities of aluminium and copper in the list of references in K. Honda's paper, *Science Reports*, Tôhoku Imperial Univers., **1**, p. 19, Sendai (Japan), 1912.

† I. Königsberger, Wiedemann's *Annal Physik.*, **66**, p. 698, 1898.

‡ K. Honda, *Annal Physik.* (4), **32**, pp. 1003–1026, 1910.

§ Pierre Weiss and Kamerlingh Onnes, *C.R.*, **150**, pp. 686–687, 1910.

|| E. Seckelson, Dissertation, Heidelberg, 1898; see also Wiedemann's *Annal. Physik.*, **67**, p. 37, 1899.

¶ P. Weiss, *loc. cit.*, designates Seckelson's statements as "assez vagues."

** Karl Ihde, Dissertation, Marburg, 1912.

†† Cp. E. Haupt, *Ges. Naturw.*, Marburg, 1904, *loc. cit.*, pp. 257 and 263.

‡‡ *Loc. cit.*

iron—that is to say, a metallographically homogeneous solution—it seems to no longer behave like a ferromagnetic body. In that case, in the presence of small proportions of iron (below 2 per cent.) no magnetisation above 0·0001 c.g.s. can magnetometrically be observed. The iron seems to act merely as a paramagnetic body and is much less disturbant than under other circumstances, though its influence cannot always be neglected when in this condition either."

We thus see that the eminently high magnetism of the Heusler aluminium bronzes can neither be explained by their impurities, nor by the extremely minimal ferromagnetism of the manganese itself. Which then is the powerful factor in these alloys? This question is to be discussed in the sections which follow.

We will in the first instance dwell upon an attempted explanation due to Guillaume,* which, we may at once state, cannot be upheld in the actual state of our knowledge.

Faraday endeavoured to account for the exceptional fact that two of the metals of the iron group, chromium and manganese, are not magnetic by the assumption that their magnetic transformation temperatures were very low. The hypothesis has never received any real experimental support; the qualitative experiments of Preusser † merely prove that the susceptibility of manganese is certainly not essentially greater at the temperature of liquid air than at ordinary temperature.

Guillaume now has suggested to make use of this unsupported hypothesis of Faraday's in order to explain the strong magnetism of the Heusler alloys. According to Faraday, manganese would, at ordinary temperature, exist in a faintly magnetic modification; but the critical magnetic point of manganese would be so much raised by the addition of Al, Sn, &c., that the strongly magnetic modification could become manifest at ordinary temperature. Guillaume was led to this assumption by the well-known fact that aluminium and tin, when alloyed with other metals, raise the melting-points of these metals.

As already indicated, this hypothesis is devoid of any experimental basis. The suggestion would, moreover, merely account for the magnetism of alloys of Al and Sn. The more general question, how to account for the high magnetic susceptibility of the other Heusler alloys, containing arsenic, antimony, bismuth or boron, would remain unanswered.

It has repeatedly been demonstrated in the experimental way, moreover, that in the case of the Al-Mn bronzes, for instance, the temperature of magnetic transformation depends upon the proportion of the aluminium contents, and the fact was, indeed, to be expected. In any case, however, the hypothesis of Guillaume is not based upon facts, and the arguments are not sufficiently supported. There is a further point which indirectly militates against the possibility of the hypothesis.

For Heusler himself has from the very first days ‡ of his discovery of the ferromagnetic manganese alloys expressed the opinion, that manganese entered into *compounds* with all the metals in question, and that the strong magnetism was constitutionally inherent in these compounds. This assumption has subsequently been entirely confirmed by the researches of Starck, Haupt, and Preusser,§ and Heusler, moreover, succeeded in fixing upon the carrier of the strong ferromagnetic properties in the Al-Mn bronzes. The magnetometric experiments of Starck and Haupt formed the first quantitative

* Ch. Ed. Guillaume, *Arch. sciences phys. et nat.*, **24**, p. 381, 1907.
† *Loc. cit.*, p. 25.
‡ See p. 180.
§ *Loc. cit.*

enquiry in this direction. All their specimens were taken from fused manganese-copper containing from 28 to 30 per cent. of manganese, to which varied proportions of aluminium were added. For the series of alloys prepared from the manganese-copper of about 30 per cent. of Mn the interesting result was established, that the maximum of magnetic susceptibility is attained when the aluminium proportion is about half that of the manganese proportion, that is to say, when the alloy contains one atom of aluminium per atom of manganese. It might, therefore, have been assumed that the magnetically active constituent was Mn_1Al_1 in a state of solid solution with copper; but the objections to this assumption were expressly stated. Heusler himself said at the time:* "There is an unmistakable analogy in the fact that, on the one hand, the salts of manganese, which is not a ferromagnetic metal, and on the other hand, certain of its alloys, display ferromagnetic properties. One might therefore feel tempted to compare the aluminium-manganese bronze to a salt solution, in which the copper would represent the solvent, and the stated combination of equal atoms of manganese and aluminium would represent the dissolved salt. . . . The tabulation of the data of Series II. does not at present show the regularities which should be expected by analogy with the salt solutions. The susceptibility (in a field of 100 absolute units, where saturation was practically reached) does not rise proportionally to the concentration, but in a steeper curve."

Definite conclusions as to the connection between magnetic properties and chemical constitution were thus not drawn in this first experimental investigation by Heusler and Haupt at that time; Heusler intended, however, to extend the research in various directions, and he was later supported in the magnetometric work by Preusser.†

The chief point was at that stage to investigate other grades of manganese-copper as to their magnetism. Experiments were therefore started with alloys which contained only 20 or 15 per cent. of manganese. The first measurements refuted the assumption which the experiments of Heusler and Haupt had suggested, viz., that there might exist in the Al-Mn bronzes solutions of the compound Mn_1Al_1 in copper, and that the degree of magnetisability depended upon the proportion of this compound Mn_1Al_1. For the alloys of *both* the series gave the maximum magnetic intensity with an Al percentage of about 13. This in the first instance rather surprising, interesting result was further confirmed by numerous measurements of specimens containing in the copper alloy 23, 10, 7·5, 3·8 per cent. of manganese; they all showed the maximum of magnetism when about 13 per cent. of aluminium was present.

These experiments seemed to furnish a basis for new theoretical speculations. Before we enter into these we should like further to elucidate the results of the measurements made by Heusler, Haupt, and Preusser by a graphical method, with the aid of the triangle of van't Hoff.‡ The three corners of this triangle signify the pure metals Al, Mn, Cu. The alloys of equal Mn-percentage lie on a parallel to the Al-Cu edge, which is indicated by an arrow. To every alloy of two or three of the components there corresponds some point in the triangle. The degree of magnetisability (saturation-intensity) may then be represented by the height of a perpendicular erected at the point. The space-curves (in the surface passed through the tops of the perpendiculars) thus obtained show, on the one side, a rise with increasing Mn-percentage at constant Al-contents, and on

* *Loc. cit.*, *Marburg Ges.*, 1904, pp. 259–260. † W. Preusser, *loc. cit.*

‡ The diagram is taken from Heusler, *Wallach-Festschrift*, *loc. cit.*, p. 472; it is printed also by Preusser, *loc. cit.*, p. 80, and in the *Zeitschr. f. anorgan. Chem.*, 61, p. 277, 1909.

the other hand, at constant Mn-percentage, a rise in the magnetisation with an increase of the Al-contents up to 13 per cent.; when the aluminium exceeds 13 per cent., the magnetisation decreases again. The elevated surface of the curves has a ridge in a straight line which runs almost parallel to the Cu-Mn edge, and points of equal magnetisability may be joined by "altitude lines"; these altitude lines apparently descend more abruptly on the left of the ridge line than they ascend on its right.

Fig. 1 shows the upper corner of the triangle and—idealised—the course of the ridge and of the altitude lines. The small circles indicate experimental determinations.

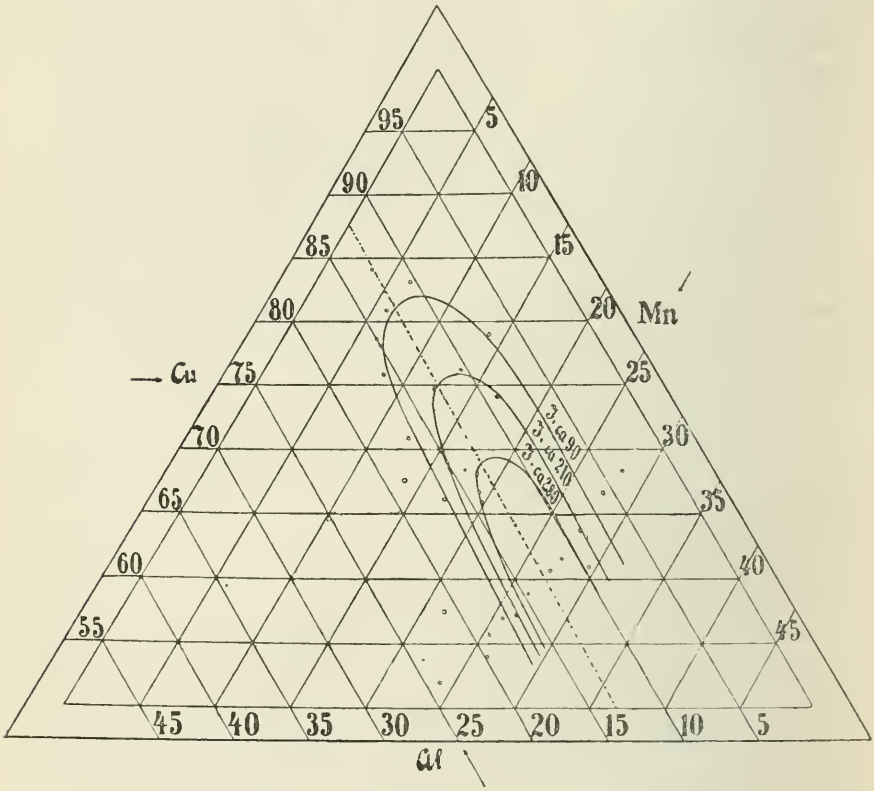


Fig. 1.

Heusler has based the following hypothesis as to the carrier of the strong ferromagnetic properties on these experiments*: "An explanation of the magnetic behaviour of manganese-aluminium-bronzes may be found by starting from the consideration: (1) That copper and aluminium form a compound $AlCu_3$; this assumption has been supported by Gwyer† in Tammann's laboratory, to whose account we should also refer readers as to the early literature; (2) that manganese and copper form a series of mixed crystals, yielding a minimum melting-point for a manganese percentage of

* *Zeitschr. anorgan. Chemie*, **61**, pp. 277–278, 1909 (received by the Editor on 3 October, 1908); see also the preliminary communication in *Ges. Beförderg. Naturw. Marburg*, 6 June, 1908, *Sitz.-Ber.*, p. 203.

† Gwyer, *Zeitschr. anorgan. Chemie*, **57**, p. 114, 1905.

about 30, as results from the experiments of S. F. Shemtshushny, T. T. Urasow, and A. E. Rykowsky.* The correctness of this statement cannot be doubted, in view of the observations made in the laboratory of the Isabellenhütte with manganese-copper alloys containing from 5 to 30 per cent. of manganese. R. Sahmen has, moreover, come to the same result." †

Heusler's opinion is now that the copper of the compound $AlCu_3$ can isomorphously be replaced by manganese, and that compounds $Al_x(Mn,Cu)_{3x}$ exist. These latter compounds he regards as the carriers of the strong ferromagnetism of Al-Mn bronzes. The letter x indicates that the magnitude of the ferromagnetic molecule cannot yet be fixed ; it may be simple in general and complex under certain conditions. It will presently be explained that the respective compound or chemical combination between aluminium and an isomorphous mixture of manganese and copper does exist, and that the total number of the manganese and copper atoms together amounts to three times the number of aluminium atoms, $Al_xCu_xMn_{(3x-a)}$.

If we accept this hypothesis, the ridge line of the diagram, Fig. 1, will mark the position of the $Al_x(Mn,Cu)_{3x}$ compounds, and it appears natural that, with constant Mn-percentage and varying Al-percentage, the maximum magnetism should correspond to the chemical compound. We further understand why, within the ridge line, the magnetism should increase with growing Mn-percentage.

In order to prevent misunderstanding, we would emphasise that the facts published in 1903 already concerning the Heusler-Haupt experimental series of alloys containing about 30 per cent. of Mn have entirely been supported by the subsequent researches, and that they likewise conform to the hypothesis which we just outlined. The 30 per cent. Mn-Cu alloy is a solid solution which accidentally contains almost exactly 1 atom of Mn to 2 atoms of Cu. The bronze of maximum magnetism of this series corresponds therefore to the compound $Al_1Mn_1Cu_2$, which will find its place in the general system $Al_x(Mn,Cu)_{3x}$.

The further examination of the hypothesis is reserved for the present. "The hypothesis," Heusler says, "seems to be of fundamental importance for the whole domain of ternary alloys. It has a parallel in the system manganese-iron-carbon, for which we assume the existence of mixed iron-manganese carbides $C_x(Mn,Fe)_{3x}$."

We would also, in this connection, call to mind the ternary *tin-manganese* bronzes, the marked ferromagnetism of which seems to be due, so far as can be stated at present, to two compounds of similar structural formulæ, as will be expounded in the following section (see p. 183).

The demonstration of the correctness of the Heusler hypothesis required above all also metallographic examination ; Richard Lorenz took up this branch of the investigation on Heusler's instigation. Microphotographic researches on Heusler alloys were described last year also by Knowlton ; ‡ he observed three kinds of crystals, one of which seemed to stand in a direct relation to the magnetometrical values. The experimental data at disposal do not yet admit, however, of gaining any deep insight into the mechanism of the phenomena.

The question as to the carrier of the strong ferromagnetism of aluminium-manganese bronzes may be considered as solved in principle, therefore, though many special points require further experimental investigation. To

* Žemczužny, Urasow, and Rykowsky, *Journ. Russ. Phys.-Chem. Soc.*, **38**, p. 1050, 1906 ; and *Zeitschr. anorgan. Chemie*, **57**, p. 253, 1905.

† Sahmen, *Zeitschr. anorgan. Chemie*, **57**, p. 20, 1905.

‡ A. A. Knowlton, *Phys. Rev.*, **32**, pp. 54–68, 1911.

Heusler is due the merit of having, on the ground of his own work and of the measurements made by his collaborators, first recognised the true nature of the Al-Mn bronzes which he discovered. I may be permitted to dwell upon this fact, because A. D. Ross* has recently advocated the same hypothesis which Heusler had, three years previously, submitted to the public

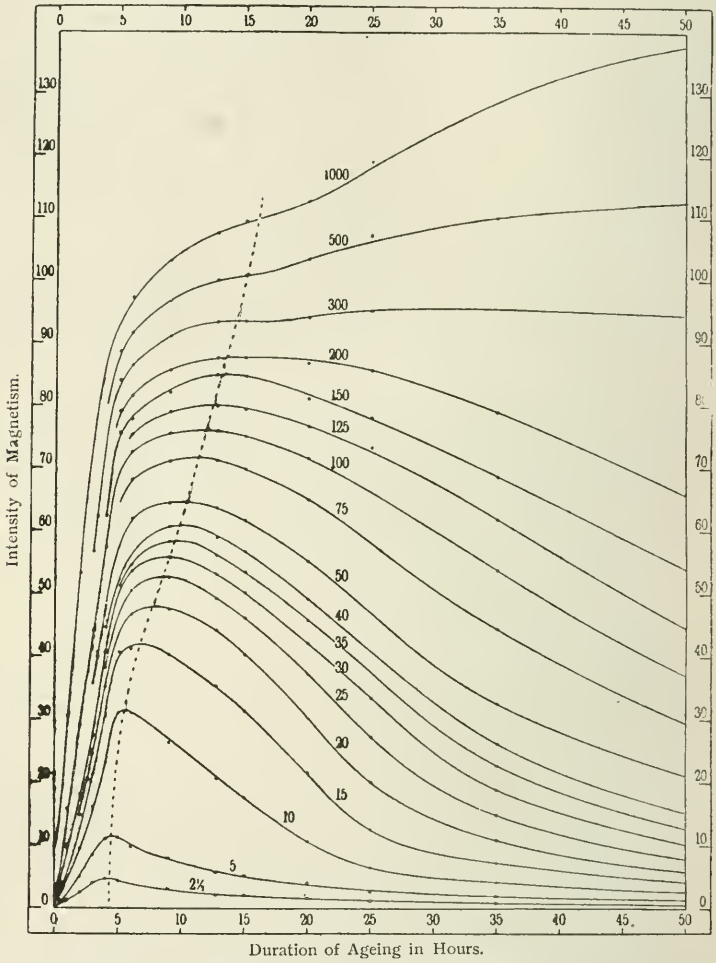


FIG. 2.—Changes in the Magnetism of a Forged Quenched Aluminium-manganese Bronze, during ageing at 209° C. Parameters, effective field intensities. Six more of these analogous plates in *Göttinger Abhandl., loc. cit.*, by E. Take.

already on a well-established basis. This statement will suffice to justify the priority claims of Heusler.

I should now like briefly to discuss a very important phenomenon which is directly intelligible from the standpoint of the expounded hypothesis. It is well known that freshly-cast Heusler bronzes are in general not at all

* A. D. Ross, *Journ. de Phys.*, (5), **1**, pp. 117–123, 1911; also A. D. Ross and R. C. Gray, *Roy. Soc. Edinb. Proc.*, **31**, pp. 85–99, 1910.

strongly magnetic; they acquire their maximum magnetic intensity by a suitable artificial ageing (by being heated for a more or less prolonged period to high temperatures).

The fact was first recognised and examined by Heusler, Haupt, and Preusser,* who conducted numerous experiments on the ageing of the aluminium-manganese bronzes, and who made important observations concerning the pronounced dependence of the magnetic phenomena upon the thermal history of the specimen. These measurements have recently been resumed by Take, and have been extended in all possible directions, consistently combined with an examination of the points of transformation. These researches have led to a large extension and also an alteration in principle of the current views on the nature of ageing. It has resulted that ageing represents a superposition of *two structural transformations*. There is (1) a development of strongly ferromagnetic elementary magnets, which is traced by measuring the increase in the saturation-magnetism; (2) there must be a further rearrangement (altogether different from the former), by virtue of which the free dirigibility of the elementary magnets (respectively of the planes of rotation of the electrons of magnetisation) is more or less impeded in the course of the ageing. This second transformation can be followed by measuring the course of the maximum limit of the coercitive force; it can also distinctly be recognised, as Fig. 2 demonstrates, by the fact that the magnetic intensities—with small and moderate field intensities the parameters—grow only during the *first* portion of the ageing period, to decrease again in a more or less marked degree after having attained a maximum, finally to approach asymptotically a stable limit.

These peculiarities are most sharply recognised in specimens which have been quenched from red glow (about 600° C.) before the initiation of the ageing. When the specimen has been cooled *slowly*, there will be sufficient time during the cooling for the formation of the strong ferromagnetic elementary magnets, as well as for the second transformation, the nature of which will further be specified in a moment. Thus the slower the cooling, the stronger the decrease in the influence of ageing.†

These are the essential qualitative features of ageing. As regards the explanation, the Heusler hypothesis furnishes us with a clear leading idea. The chemical compound $Al_x(Mn,Cu)_{3x}$ is the carrier of the strong ferromagnetism. This supposition forces the idea upon us that at high temperatures the relatively complex compound $Al_x(Cu,Mn)_{3x}$ is dissociated into more or less large fragments, which themselves may be in a state of solid solution with the rest of the alloy, and that the formation of strong ferromagnetic elementary magnets which occurs during the ageing of quenched specimens (or during the slow cooling from high temperatures) takes place only by an association of the constituents to this compound $Al_x(Mn,Cu)_{3x}$. A modified interpretation of the facts would also be admissible. Various recent researches‡ in the field of ferromagnetic alloys point to the view that *ferro*magnetism is not a property inherent in *single* molecules at all, but that a special space-lattice structure is a necessary condition for its appearance. In our case we might

* *Loc. cit.*

† This observation was confirmed, after the completion of Take's experiments, by Ross and Gray, *Zeitschr. anorg. Chemie*, **63**, p. 349, 1909. It had moreover long been known to Heusler that *slowly* cooled cast bronzes were pretty strongly magnetic after cooling already, and that they were little improved by ageing.

‡ K. Honda, *Annalen Physik.*, (4), **32**, pp. 1003–1026, 1910; Loutchinsky, *C. R.*, **148**, pp. 1759–1760, 1909; S. Hilpert, *Verh. Deutsch. Physik. Ges.*, **11**, pp. 293–209, 1909; Pierre Weiss, *Zeitschr. f. Krystallogr.*, **29**, pp. 411 and 690, 1898. See also the résumé by E. Take in the *Göttinger Abhandl.*, *loc. cit.*, pp. 97–98.

therefore assume that the marked ferromagnetism of the Heusler Al-Mn alloys will only then become manifest when the separate $Al_x(Mn,Cu)_{3x}$ molecules, having been re-formed from dissociated fragments, are further united, by segregation from the solid solution, to a crystalline aggregate of quite a definite kind. Which of these views is in harmony with the facts, cannot be decided yet. We will therefore merely speak of ferromagnetic *elementary* magnets in quite a general manner.

The recent investigations of Take demonstrate, however, that there exists a second modification of the structure which is essentially different from the first, and as a result of which the free dirigibility of the ferromagnetic elementary magnets is much impeded as the ageing period is prolonged. This second change in the constitution may, according to Take, be regarded as a complex formation between the separate elementary magnets.* This idea leads back to a previously made suggestion of Richarz for the explanation of the experiments of Heusler and Asteroth (presently to be alluded to again), according to which an alloy will contain all the larger complex molecules, the slower the cooling from a temperature lying above the critical magnetic point. This view implies that slow cooling and artificial ageing of quenched specimens are essentially the same processes, in so far as they are both based on the same tendency in the development of the internal structure. Artificial ageing would hence merely call forth, by the aid of heat movements, a release of undercooled, labile conditions, as was generally pointed out by Heusler already in his first publication concerning this subject. Yet Take has demonstrated that ageing experiments made with the same bronze at different temperatures do *not* all lead to the *same* stable final result. The final conditions, indeed, vary strongly when the temperature of ageing varies. Ageing, moreover, seems to lead, under certain circumstances, to still more stable conditions than have ever been obtained experimentally with the slowest cooling. This results from Take's measurements of the maximum coercive force. This force amounted, *e.g.*, in the case of a malleable Heusler bronze, after 16 hours' cooling from 800° C. down to ordinary temperature, only to 26·8 Gauss, whilst the coercive force of the same specimen could be raised to 167·6 Gauss by quenching at 600° C. followed by a suitable ageing (for details see *Götting. Abhandl.*), at a temperature *above* the original temperature of magnetic transformation. This latter coercive force represents about twice the coercive force observed in the hardest magnet-steels.

We see, therefore, how the whole domain of the important ageing phenomena, which we observe in the aluminium-manganese alloys, becomes at once intelligible from Heusler's point of view concerning the carrier of strong ferromagnetism. We have already mentioned the special case—discovered by Heusler† already in 1905, and subsequently quantitatively

* The *two* modifications of ageing are distinctly indicated also by the change in the specific heat, as Dippel ascertained (*loc. cit.*). Manganese bronze was first quenched at 600° C. and then aged; as the ageing proceeded, there resulted first an increase, and then a large decrease in the specific heat. The appearance of a maximum would, according to Take (*Götting. Abh., loc. cit.*, p. 125) simply be explained by the superposition of the two structural transformations of the ageing period. The development of the ferromagnetic elementary magnets is connected with an increase in the specific heat (Take); the second structural change in the complex compounds must, on the other hand, be accompanied by a decrease in the specific heat (kinetic theory of Richarz). The variations observed by Dippel would hence be a differential effect; in the beginning of the ageing period the specific heat will mainly be influenced by the elementary magnets; at later stages the influence of the complex formation will predominate.

† Heusler, *Marburger Sitz. Ber.*, November, 1905, *loc. cit.*

confirmed by Asteroth * and explained by Richarz †—that heating above the point of magnetic transformation, *quenching* and ageing result in small coercive force and small hysteresis, whilst *slow* cooling and ageing result in large hysteresis. This is particularly noticeable in the malleable aluminium-manganese bronzes.

The carrier of the marked ferromagnetism in the aluminium-manganese bronzes is therefore, according to Heusler, the chemical compound $Al_x(Mn,Cu)_{3x}$. How it is that just this chemical compound gives rise, all at once, to the appearance of strong magnetic properties, we do not know so far. Richarz, Weiss, and Take have, however, thrown out hypotheses for the possible explanation of the phenomena.

In connection with his explanation of the atomic magnetism by the rotating elementary quanta of Helmholtz,‡ Richarz has indicated how the ferromagnetism of the Heusler alloys might be understood in several ways.§ It would in the first instance be possible ‖ that the formation of the elementary magnets during ageing might depend upon constitutional changes in the structure, such that electrons within the molecular aggregates were caused to rotate which previously had not been rotating. It would, secondly,¶ be conceivable that, under strongly magnetic conditions, magnetisation-electrons might be present which rotated with a higher speed or in larger orbits than in a weak magnetic state. A third possibility,** to which Weiss †† had also drawn attention, would be that the circulation of some elementary quanta or the dirigibility of the rotating elementary quanta should, in the manganese atom, as a rule be impeded by the neighbouring elementary quanta, being electrically charged in the opposite sense, and that this impediment would be removed in the Heusler alloys by the presence of compounds between the manganese atom and the atoms of aluminium and copper.

Weiss has expressed this latter view in the following words: "On peut, pour un corps magnétique, concevoir deux manières de ne pas être ferromagnétique ou . . . ou bien, le champ moléculaire existant, les molécules sont bloquées par d'autres forces qui les empêchent de tourner. On peut se demander si tel ne serait pas le cas du manganèse aux molécules duquel les métaux étrangers, l'aluminium et le cuivre, rendraient en les écartant leur mobilité."

Finally, we will refer to another possible explanation, to which Take has pointed ‡‡: Langevin §§ assumes that every molecule of a paramagnetic or a ferromagnetic body has a magnetic moment which differs from zero and which results from the geometrical addition of all the separate magnetic moments produced by the totality of the electrons circulating within the

* P. Asteroth, *loc. cit.*

† Compare Asteroth, Dissertation, Marburg, 1907.

‡ *Sitz. Ber. Niederrhein. Ges. zu Bonn*, December 4, 1893; *Sitz. Ber. Münchener Akad.*, **24**, p. 3, 1894; Wiedemann's *Annal. Physik.*, **52**, p. 410, 1894.

§ Richarz has pointed out that each of his assumptions presumes for the magnetic state that certain electrons possess an increased mobility. He concludes that a relation should exist in the case of the Heusler alloys between magnetic susceptibility on the one hand, and electric conductivity and thermoelectric properties on the other. The experiments of F. A. Schulze (*loc. cit.*) have confirmed this assumption in its essential features.

‖ *Zeitschr. anorgan. Chemie*, **61**, p. 271, 1909.

¶ F. Richarz, *Physik. Zeitschr.*, **12**, p. 155, 1911.

** Compare W. Gebhardt, Dissertation, Marburg, 1909, pp. 35-36, and F. Richarz, *Congrès de Radiologie et d'Electricité*, Brussels, C. R., 1911, p. 623.

†† Pierre Weiss, *Journ. de Phys.*, (4), **6**, p. 689, 1907.

‡‡ E. Take, *Göttinger Abhandl.*, *loc. cit.* pp. 99-100.

§§ Langevin, *Ann. Chim. Phys.*, (8), **5**, pp. 70-127, 1905.

molecular system. The appearance of strong ferromagnetism during ageing might then be conceived as follows: there are present, already before the ageing, in the single, still separated bricks of the elementary magnets, and particularly perhaps in the atoms of manganese, a certain number of rotating electrons; they move in such paths, however, that the magnetic moments of the single bricks of what will afterwards constitute the strongly magnetic elementary magnets only yield an additive resulting moment which will be very small so far as the exterior is concerned. When the strongly magnetic elementary magnets are being built up, be that by ageing or by slow cooling, the separate orbits of the circulating magnetisation-electrons are deformed or mutually displaced by a rearrangement, such that the resulting compound $Al_x(Mn,Cu)_3$, shows a very large resultant total moment.

Part II.

THE PROPERTIES OF THE ALLOYS OF MANGANESE WITH BORON, ARSENIC, ANTIMONY, BISMUTH, AND TIN.

By Dr. Fr. Heusler.

As I stated already on another occasion,* I inclined, after discovering the ferromagnetic manganese alloys, at once to the opinion that the phenomena would have to be explained by the assumption of a formation of chemical compounds when manganese or manganese-copper are alloyed with tin, aluminium, arsenic, antimony, or boron. When I began to investigate this subject systematically, in 1898–99, it was a matter of course for every chemist to assume that arsenic, antimony, and boron would chemically combine with the metals with which they are alloyed. There was doubt, however, as regards aluminium, tin, and bismuth. For Tammann's work was not yet known in those days, and the opinions which other investigators held before Tammann concerning chemical compounds between metals were not free from doubt.

I therefore thought that a magnetometric enquiry into the properties of the alloys which bear my name might reveal their constitution. Alloys which could be cast in the shape of compact rods, and which possessed relatively strong magnetism, seemed to be best suited for this purpose. Such were the ternary alloys of manganese-copper with aluminium and tin. The first measurements made displayed strong variations, however, caused by the history of the alloys. It was hence necessary, in the interest of arriving at a definite decision in the enquiry into the constitution of the ferromagnetic alloys, to conduct very extensive series of experiments with alloys of manganese, copper, and aluminium. The results of these experiments have been communicated by Take in the first part of this paper, and I will only add that the excellent work of this young investigator has rendered the malleable Heusler bronze (manganese-aluminium-copper, containing about 15 per cent. of Mn and 10 of Al) one of the best-known ternary metallic alloys. I am now in a position to bring my own researches on this material to a conclusion, and I shall soon report on the results, which will elucidate the relation between structure and magnetic properties.

The long, but sure way which I have followed in my investigations has evidently not been understood. Thus it is that Hilpert and Dieckmann,†

* *Wallach-Festschrift*, 1909, pp. 467–477 (Göttingen, Vandenhoeck and Ruprecht). See also *Chem. Zentralblatt*, 1909, ii., p. 1529.

† *Ber. Deutsch. Chem. Ges.*, 44, p. 2831, 1911.

e.g., remark that ternary and quaternary systems had often been investigated, and that it was difficult to draw definite conclusions, because the positions of the transformation points were strongly dependent upon the previous treatment of the materials. I myself must say, on the contrary, that I have just for this reason not seen much more than preliminary experiments in almost all the researches which have so far been published concerning alloys of manganese with arsenic, antimony, bismuth, and perhaps even with boron. For all these researches measure the magnetic qualities of preparations without heeding the possibility that these alloys might likewise exist in different modifications. After having demonstrated, in conjunction with Haupt, Preusser, and Take, with regard to Mn-Al-Cu, and in conjunction with Fassbender with regard to Mn-Sb and Mn-Sn, that the history of the specimens had a decided influence upon the kind and intensity of the magnetism, I consider that exhaustive investigations of any ferromagnetic alloys must pay full attention to these first problems before any conclusions as to the chemical constitution can justifiedly be drawn from the magnetic properties.

I thus come to the persistent attempts made by E. Wedekind (compare his book: *Magnetochemie*, Berlin, 1911 : Gebr. Borntträger) to characterise my observations as accidental and to ascribe to himself the merit of having recognised that the marked ferromagnetism of the alloys of manganese and of manganese-copper with As, Sb, Bi, B, Al, Sn is a molecular quality. *I have, in the Wallach-Festschrift, expressly claimed this conclusion as my spiritual property*, and I regret that Wedekind believes he can dispose of this reclamation by omitting all reference to it in his book. I also regret, after having repeatedly been obliged to establish my priority with respect to Wedekind and to other investigators, that Wedekind has recently again published a paper on manganese-bismuth,* in which he does not make any mention whatever of the fact that I announced the magnetism of manganese-bismuth as early as 1902, and that I drew particular attention to the interesting formation of a ferromagnetic alloy consisting of manganese and diamagnetic bismuth.

From a chemical standpoint the following may be remarked with respect to the ferromagnetic alloys or compounds of manganese with boron, arsenic, antimony, bismuth, and tin.

Manganese-boron.—I stated in 1901 and 1903 that this alloy has magnetic properties. It is a curious incident that this observation escaped such distinguished scientists as Troost and Hautefeuille. For I have prepared the manganese boride by their method (and also by other methods), by melting manganese carbide with boric anhydride, and I have found it magnetic. Binet du Jassoneix,† who likewise experimented with manganese-boron in 1904, and Wedekind ‡ himself, who described the substance in 1905, that is, two years after the publication of my first experiments, did not notice the strong ferromagnetism of manganese-boron. I drew Wedekind's attention to this interesting property in a letter which I addressed to him. In reply, Wedekind read, four weeks later, a paper before the Deutsche Bunsengesellschaft § which caused my first reclamation. Wedekind represented the case as if he had gone one step further than myself, because he was dealing with chemical obtained from a 30 per cent. manganese-copper and aluminium, the compounds (I had long before established and published that in the alloys

* *Ber. Deutsch. Chem. Ges.*, 44, p. 2831, 1911.
† *C. R.*, 139, p. 1209, 1904.
‡ *Ber. Deutsch. Chem. Ges.*, 38, p. 1228, 1907.
§ *Zeitschr. Elektrochem.*, 1905.

maximum magnetism was reached when there existed a definite atomic relation between Al and Mn; I had thus proved that *chemical combination was taking place*). I wish to state that Wedekind at that time had nothing but impure preparations at his disposal. It is the merit of Binet du Jassoneix* to have produced, in addition to the MnB_2 of Troost and Hautefeuille, which is almost non-magnetic in the pure state, the pure compound MnB, and to have established that the latter compound is the carrier of the ferromagnetism. I must assume from the results of Jassoneix that the manganese boride which I prepared after Troost and Hautefeuille was a mixture of MnB and MnB_2.

Manganese-arsenic.—I stated in 1901 and 1903 that the alloy manganese-arsenic is magnetic. Wedekind† contradicted, but wrongly, for the body which he prepared and described as a chemical compound MnAs and as non-magnetic, yields far below red glow arsenious vapours when heated in a test-tube and turns ferromagnetic. This observation, which I have not published so far, has in a somewhat different form also been made by Hilpert and Dieckmann,‡ and has later been confirmed by Wedekind.§ The manganese arsenide, MnAs, of Hilpert and Dieckmann‡ is very remarkable; it offers the greatest probability of all ferromagnetic alloys of really being a chemical individual. Unfortunately it could not be fused magnetometrically to be examined in compact lumps. This arsenide MnAs shows the maximum magnetism (Hilpert and Dieckmann).

The existence of the compound Mn_2As which Wedekind and Veit recently described is strongly doubted by Hilpert and Dieckmann.

Manganese-antimony.—Having noticed that both manganese and manganese-copper become ferromagnetic when alloyed with antimony, I induced Fassbender‖ to conduct magnetometric tests. His specimens were compact fused lumps which could not be machined, however, and the test had hence to be made with powders. All the specimens were aged; some specimens were also tested before ageing, being quenched in cold water from red heat; these experiments were not conclusive, however, especially because Fassbender did not possess any alloys of high manganese percentage. I would, therefore, refer readers to the research which Rob. S. Williams¶ carried out in Tammann's laboratory. He established the existence of the compounds Mn_2Sb and Mn_3Sb_2 and found qualitatively that the former corresponds to the maximum of magnetism.

Williams expressly contests the existence of the compound MnSb which Wedekind had claimed. Hilpert and Dieckmann** have recently discussed the existence of this MnSb and also tried to prepare it from amalgam. They do not appear, however, to have established the existence of this compound.

Manganese-bismuth.—Both manganese and manganese-copper, I showed in 1902 and 1904, yield ferromagnetic alloys with bismuth. I have not been able yet to make magnetometric tests. The alloys of manganese and bismuth which Wedekind†† and Hilpert and Dieckmann** have prepared, have not yet been tested magnetometrically either.

Manganese-tin.—Some manganese-tin which the Isabellenhütte had to

* *C. R.*, **142**, p. 1336, 1906; *Ber.*, **40**, p. 3193, 1907. See also Wedekind, *Ber.*, **40**, p. 1259, 1907.

† *Zeitschr. Elektrochem.*, **11**, p. 850, 1905.

‡ *Ber.*, **44**, p. 2378, 1911.

§ *Ibid.*, **44**, p. 2663, 1911.

‖ *Verh. Deutsch. Physik. Ges.*, **10**, p. 256, 1908.

¶ *Zeitschr. anorgan. Chem.*, **55**, p. 1, 1907; as to the measurements see also Honda, *Annal. Physik.* (4), **32**, pp. 1003–1025, 1910.

** *Ber.*, **44**, p. 2831, 1911.

†† *Ibid.*, **44**, p. 2663, 1911.

supply for an English firm many years ago gave me the opportunity of experimenting with this alloy, and it was then that I discovered the production of a ferromagnetic alloy from non-magnetic metals. When I later on took up the systematic study of these phenomena I ascertained, in the first instance—

1. That manganese-tin remains magnetic when further alloyed with copper ;

2. That manganese-copper turns magnetic when tin is introduced.

These two facts seemed to be explicable only by the assumption (see *Wallach-Festschrift*, p. 468) that chemical reactions were taking place. Manganese-tin was subsequently studied by R. S. Williams,* who believes in the existence of two compounds, Mn_4Sn and Mn_2Sn, of which he found the former in qualitative tests particularly magnetic.

On my instigation Fassbender made measurements, in connection with the previously mentioned tests, with the powdered material, and he also found the maximum magnetism in Mn_4Sn.

During his long collaboration with me Haupt has taken magnetometric measurements of some rods of an alloy of manganese-copper (30 per cent. of Mn) with tin which I had prepared. A maximum magnetism was observed in the alloy containing about 18 per cent. of Sn. Recently Ross and Gray † prepared a further series of alloys of the 30 per cent. manganese-copper with tin and submitted them to magnetometric tests. They observed a second more pronounced maximum for a tin contents of about 38 per cent. The observation does not come unexpectedly to me ; it would support an assumption of mine which I shall enunciate as soon as I have proofs for it.

Part III.

GENERAL SUMMARY.

1. In order to account for the pronounced ferromagnetism of the Heusler alloys, aluminium or tin-manganese bronzes, Guillaume assumes with Faraday that pure manganese exists in a strongly magnetic modification, which undergoes transformation at a very low temperature ; this temperature is said to be raised by the addition of Al or Sn, so that the magnetism of these alloys becomes apparent. This hypothesis is not based upon facts, and the arguments are not sufficiently supported ; it would, moreover, not explain the strong ferromagnetism of the Heusler manganese alloys with As, Sb, Bi, and B.

2. Heusler, on the other hand, has advanced a hypothesis which perfectly explains all the phenomena ; for he has not only discovered the ferromagnetic manganese alloys, but he also first proved, in 1903, that the appearance of the strong ferromagnetism is due to the formation of chemical compounds, and that the ferromagnetism is thus a molecular phenomenon.

Priority of Heusler with respect to Wedekind.

3. It is stated and demonstrated in detail which these strongly ferromagnetic chemical compounds are. (Heusler, Haupt, Preusser, Williams, Ross, Hilpert.)

4. The research above explained proves the Heusler Al-Mn bronze to be,

* *Zeitschr. anorgan. Chem.*, 55, p. 1, 1907.
† *Roy. Soc, Edinb. Proc.* 31, pp. 85–99, 1910.

in physical respects, an exceedingly interesting material of valuable properties, especially as regards hysteresis.

4*a*. By the process described by Heusler the malleable Al-bronzes in particular can be converted into an unmagnetic modification which, suitably aged, yields a strongly magnetic material of very small hysteresis (Heusler, Asteroth, Take).

4*b*. By the method of Take the malleable Al-bronzes in particular may, by another ageing process, be transformed into a permanently magnetic modification of exceedingly high intensity.

5. Hypotheses for explaining the strong ferromagnetism of the chemical compounds on the electron theory have been suggested by Richarz, Weiss, and Take.

6. The physical properties mentioned under 4*a* are due, according to Richarz, to a very slight formation of complexes of the elementary magnets in the one case, and to a very pronounced formation of such complexes in the other case.

7. According to his experiments the phenomena of ageing are due, according to Take, to *two* transformations ; the first transformation is the gradual formation of the strong ferromagnetic compound of Heusler ; the second is the gradual complex formation, also suggested by Richarz with regard to the experiments by Heusler and Asteroth. This complex-formation also gives rise to the enormous coercive forces which are observed in the case 4*b*.

ON THE MAGNETIC PROPERTIES AND MICROSTRUCTURE OF THE HEUSLER ALLOYS.

Dr. Alexander D. Ross, M.A., D.Sc., F.R.S.E. (Lecturer on Natural Philosophy in the University of Glasgow) read a Paper "On the Magnetic Properties and Microstructure of the Heusler Alloys."

Although almost all substances exhibit in at least a very feeble degree the phenomenon of magnetism, yet iron, nickel, cobalt, and certain of their alloys are, generally speaking, the only materials which show magnetic quality in a pronounced manner. The amount of magnetism which may be induced in such metals is relatively enormous, and the fact that this magnetism is to some extent permanent (remaining after the removal of the magnetising force) places these bodies in a class by themselves. They are said to be ferromagnetic. The term is here used in contradistinction to that of paramagnetic, which is applied to materials capable of acquiring induced magnetism but exhibiting no retentivity.

There are, however, certain ferromagnetic alloys and compounds the constituent elements of which are practically non-magnetic; that is to say, they are built up from substances which show at the most only a feeble induced magnetism and very little or no residual magnetism. The first compound of this type to be discovered was the oxide of chromium, Cr_5O_9.* In 1903 Heusler announced† that many binary and ternary manganese alloys exhibit decided ferromagnetic properties. Thus alloys of manganese with aluminium, tin, antimony, bismuth, boron, and arsenic are all magnetic, and some of the ternary alloys of manganese and aluminium with copper show a saturation intensity of magnetisation exceeding three-fourths of that of pure nickel. They also exhibit retentivity, especially after certain forms of heat treatment. The ternary alloys of copper, manganese, and aluminium—commonly referred to as Heusler alloys—have aroused much interest, and the united work of many experimenters has resulted in the collection of a large amount of data regarding their magnetic, electrical, optical, and elastic properties. The other groups of magnetic alloys have not yet been examined in such detail.

The author has been engaged for some time on investigations into these groups of binary and ternary alloys, especially as regards their magnetic properties. Other systems of alloys have also been examined, in so far as it was thought likely that the results so obtained might throw light on these peculiar ferromagnetic substances. Several papers have been published during the progress of these researches, but now that the magnetic investigations are practically completed, one is in a position to review the behaviour of this class of alloys when taken as a whole, and to derive therefrom important

* F. Wöhler, *Lieb. Ann.*, cxi., 117, 1859.

† F. Heusler, *Verh. d. deutsch. phys. Ges.*, v., 219, 1903; *Schrift. d. Ges. z. Beförd. d. Ges. Naturw. z. Marburg*, xiii., 255, 1904.

general inferences regarding the origin of the magnetic properties. Moreover, the metallographic examination of the structure of some of these alloys, which has recently been taken in hand, has already afforded valuable evidence in support of certain hypotheses first advanced by the author three years ago, and it has done much to explain the behaviour of the alloys under varied heat treatment. At the same time the investigations have opened up some problems of general interest regarding the relations which exist between magnetic properties and metallographic constitution, and the solution of these must have an important bearing on a theory of magnetism.

Magnetic tests have been carried out on alloys belonging to the following groups :—(1) Copper-manganese-aluminium, (2) copper-manganese-tin, (3) copper-manganese-antimony, (4) copper-manganese-bismuth, (5) copper-manganese, (6) copper-aluminium, (7) manganese-antimony, (8) manganese-boron. The first two series were examined in considerable detail, a large number of castings having been prepared in each group. Sets 3 and 4 have only been investigated to such an extent as to bring out the similarities and differences existing between them and the previous groups. The binary alloys have been tested in only a comparatively few specimens, with the exception of the copper-aluminium group, which has been very fully examined by Mr. R. C. Gray in a research carried out under the author's supervision.

Every effort has been made to obtain materials of the highest purity for the preparation of the specimens. The copper was the best electrolytic metal and contained less than 0·15 per cent. total impurity, while the aluminium, obtained from the British Aluminium Company, was a specially pure sample containing not more than 0·4 per cent. of impurity. Difficulty was experienced in getting pure manganese. The metal which is commonly sold as pure manganese contains as a rule 3 or 4 per cent. of foreign matter, and has often a considerable iron content. The metal employed in the research was prepared by the Thermit process and contained about 98·5 per cent. of pure manganese, the remainder being principally silicon, aluminium, and iron, along with a trace of nickel. It is to be noted that silicon forms a magnetic alloy with manganese, but when present as only a fraction of 1 per cent., the resultant magnetic quality is very slight. Still it may have influenced the results obtained in the case of the copper-manganese binary alloys, although its effect would be altogether inappreciable in the ternary series. The iron impurity is of little moment, as experiments have shown that the addition of a small quantity of iron to Heusler alloys does not perceptibly alter the permeability. The great advantage gained by the use of thermit manganese is the very low carbon content. This is very important, as the presence of carbon has a powerful influence in modifying the equilibria of manganese alloys and even in altering the magnetic and other properties of manganese itself. The specimens of manganese-boron alloys were prepared in an electric furnace by a German firm, as the appliances at the author's disposal were insufficient to permit of his carrying out the work himself. The materials employed were not analysed, and it is possible that they may have contained a much greater admixture of foreign matter than those referred to above.

In the preparation of the ternary alloys the method adopted was to make first a 30 per cent. manganese-copper alloy. The copper was melted in a "Salamander" crucible under a layer of fused barium chloride. The proper amount of manganese was then added, and the heating continued for some time. The crucible was then removed from the furnace, the contents carefully stirred, and, while the metal cooled to the desired casting tempera-

ture, the surface was skimmed. The alloy was then poured into a series of dry sand moulds which had been lined with whiting.

In the second part of the process the third metal was alloyed in the same way with this cupro-manganese. Some difficulty was experienced at first in obtaining thoroughly satisfactory castings. If the alloys are allowed to stand before casting there is a risk of segregation occurring. On the other hand, if the stirring is continued up to the time of casting, a porous structure may result. When the appearance of the alloy, or the chemical analysis of test pieces taken from the top and bottom of the rods, indicated any deviation from homogeneity, the material was again melted up and recast. In the analysis tin was estimated in the form of stannic oxide, copper as copper sulphide, and aluminium as aluminium oxide. The alkaline manganiferous filtrate from which the other metals had been removed was made alkaline with excess ammonia, and the hydrated peroxide of manganese precipitated by the addition of bromine water. The precipitate was afterwards converted into Mn_3O_4 and estimated as tetroxide.

The primary object of the magnetic tests on the ternary alloys was fourfold: (1) To determine the magnetic quality of the alloys in the condition as cast; (2) to ascertain the best thermal treatment for bringing the alloys into a stable condition with maximum permeability; (3) to test the variation

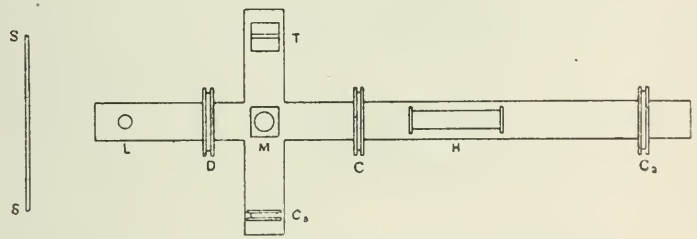


FIG 1.—The Gray-Ross Magnetometer (Plan).

of permeability with temperature in the alloys; and (4) to investigate the effects of annealing and quenching the metals at various temperatures. As some of the alloys to be experimented upon were very feebly magnetic, the necessity arose for special testing apparatus of high sensitiveness. Magnetometric methods were preferable, as in them alone is the behaviour of the specimen directly under observation during the carrying out of a test. An instrument was finally designed by Dr. J. G. Gray and the author which has been described in detail elsewhere,* and whose essential parts need only brief reference in this paper. The magnetometer is shown in plan in Fig. 1. It is built on a strong mahogany base-board, constructed in the form of a cross. On it are mounted in channelled beds the various coils, which can all be fixed in any desired places by means of friction clamps. *M*, the magnetometer proper, consists of a small magnet 7 mm. long, carrying a concave mirror, and suspended by a long quartz fibre. The lamp *L* is fitted with a fine cross-wire, the image of which is thrown by the mirror *M* on the engine-divided glass scale *SS*. *H* is the magnetising helix or solenoid, wound with four layers of insulated copper wire on a thin brass water-jacket, which keeps the wire cool even when the electric heating furnace is introduced. The coils, C_1, C_2, C_3, are connected up in series with the helix *H*, and are so

* J. G. Gray and A. D. Ross, *Proc. Roy. Soc. Edin.*, xxix., 182, 1909, and *Phil. Mag.* 6, xviii., 148, 1909.

adjusted as exactly to neutralise at the needle the effect of the current in H. C_1 almost gives complete compensation, but, as a slight error in setting it, or a slight and almost unavoidable displacement in clamping it, produces a considerable effect at the needle, the distance coil C_2 is used as a fine adjustment. Coil C_3 annuls any error arising from a deviation of the axes of the coils H, C_1, and C_2 from the magnetic east-and-west line. D is a damping coil connected up with a cell and reversing key and enables the magnetometer needle to be brought rapidly to rest. For maintaining specimens at a high temperature during the progress of a test, an electric furnace is slipped within the solenoid. The type of furnace used was one designed by Dr. Gray and the author,* which enables the alloys to be raised to temperatures approaching their melting-points without chance of their oxidation. Arrangements were also devised † whereby the specimens could be kept immersed in liquid air while in the solenoid, thus enabling the metals to be tested at 190° C.

It is proposed in the present paper to summarise the general results of the magnetic tests on the various classes of alloys, referring to published papers for details where these have been previously announced. As typical of the class of copper-manganese-aluminium alloys, ‡ the alloy No. 22, containing 62 per cent. copper, 25 per cent. manganese, and 8 per cent. aluminium, will be discussed, and as representative of the manganese-tin bronzes,§ the alloy No. 35 of 43·4 per cent. copper, 18·1 per cent. manganese, and 40·0 per cent. tin. When these materials were tested in the condition as cast, it was found that the aluminium alloy showed a large enhancement of permeability on cooling from 15° C. to — 190° C., whereas the tin alloy has a permeability almost independent of the temperature at which the test is carried out. This is shown in the accompanying table, which gives the permeability at 15° C.

Variation of Permeability with Temperature.

Applied Field H.	Permeability.			
	Cu + Mn + Al Alloy. No. 22.		Cu + Mn + Sn Alloy. No. 35.	
	15° C.	— 190° C.	15° C.	— 190° C.
20	161	189	13·2	13·2
50	74	91	13·3	13·3
100	40	50	11·9	11·9
200	21	26	10·0	10·1

and — 190° C. for various values of the applied field. At the same time it is to be noted that some of the manganese-tin bronzes show an improvement in quality on cooling to liquid air temperature, just as do the copper-manganese-aluminium alloys. Thus alloy No. 32, which contained 58·7 per cent. copper, 23·5 per cent. manganese, and 16·1 per cent. of tin, had its permeability corresponding to H = 100 c.g.s. units increased by over 25 per cent. when the metal was cooled from room temperature to — 190° C. An important fact to

* J. G. Gray and A. D. Ross, *Proc. Roy. Phil. Soc. Glasgow*, xli., 84, 1910.

† A. D. Ross, *Proc. Roy. Soc. Edin.*, xxvii., 88, 1907.

‡ For details see the following papers by the author : *Proc. Roy. Soc. Edin.*, xxvii., 88, 1907 ; *ibid.*, xxix., 274, 1909 ; *Zeitschr. f. anorg. Chem.*, lxiii., 349, 1909.

§ For details see the following papers by the author : *Proc. Roy. Soc. Edin.*, xxxi., 85, 1910 ; *Journ. de Phys.*, **5**, i., 117, 1911.

note is that in every case where an improvement in quality is found, it occurs for all values of the applied field. This behaviour is in marked opposition to that of ferrous alloys. Iron, carbon steels, and steels containing silicon, aluminium, tungsten, chromium, vanadium, &c., show enhanced permeability at liquid air temperature only for high values of the applied field. For smaller magnetising fields the magnetic induction is less at — 190° C. than at room temperature, so that the B-H curves corresponding to 15° C. and — 190° C. cross one another.* Such crossing does not occur in the case of any of the bronzes described in the present paper.

The effect of exposure to heat is very pronounced in these copper alloys. If the metal is raised to about 180° C. and gradually cooled back to room temperature, any strains in the metal due to the comparatively rapid cooling in casting are removed, and the metal is now in a normalised condition. This normalising process is found to produce very little change in the copper-manganese-aluminium alloys, but the copper-manganese-tin alloys are generally brought thereby into a more magnetic condition. The shape of the B-H curve remains unaltered, but the ordinates giving the values of B are increased in many cases by several per cent. Baking the alloys at 180° C. increases the permeability, but if the heating is prolonged the coercive force augments rapidly, so that the increased hysteresis more than counterbalances any improvement obtained through increased permeability. The alloys are brought into their best magnetic condition by heating to 180° C., and gradual cooling therefrom, the temperature of 180° being maintained for six to eight hours in the case of the copper-manganese-aluminium alloys, and only for a few minutes in the case of the tin alloys.

The copper-manganese-antimony alloys behave very similarly to copper-manganese-aluminium alloys. The copper-manganese-bismuth alloys are, however, peculiar in that cooling to liquid air temperature diminishes the permeability and annealing renders the quality inferior.†

Quenching any of these ternary alloys results in diminished permeability and diminished coercive force, with the single exception of the bismuth group, which again behave in exactly the reverse manner to the others. Fig. 2 shows the manner in which the permeability (corresponding to H = 20) of the copper-manganese-aluminium alloy No. 22 varies with the temperature at which the metal has been quenched in ice-cold water. The lower curve gives the permeability measured at room temperature, the upper curve that measured at — 190° C. It will be seen that there is a decided minimum at 610° C., indicating some structural change at that temperature. The remarkable result is that these quenched alloys are in a labile state. If left for a long time at room temperature the metal undergoes a slow transformation by which the permeability gradually returns in the course of a year to almost its original value, while the hysteresis does not increase. The process therefore results in the preparation of a metal with fair permeability ($\mu = 160$ for $H = 20$) and almost no hysteresis (coercive force less than 0·3 c.g.s. unit). This remarkable fact was first pointed out by the author in 1906,‡ and Asteroth has since shown § that the recovery of magnetic quality can be accelerated by exposing the quenched alloy to a temperature of about 150° C.

By baking the alloys at various temperatures, the quality undergoes peculiar

* Cf. paper communicated at this meeting by Dr. J. G. Gray and the author "On the Magnetic Properties of a Variety of Special Steels at Low Temperatures."

† A. D. Ross, *Journ. Inst. of Metals*, No. 2, iv., 80, 1910.

‡ Ibid., and *Proc. Roy. Soc. Edin.*, xxvii., 88, 1907.

§ P. Asteroth, Inaug. Diss., Marburg; *Verh. d. deutsch. Phys. Ges.*, x., 21, 1908.

variations, pointing to important structural changes. Fig. 3 shows how the intensity of magnetisation of the copper-manganese-aluminium alloy No. 22 varies when the metal is tested at 15° C. and at — 190° C., after having been baked for periods of three hours at various temperatures ranging from 80° to 480°. The continuous curves correspond to tests at room temperature,

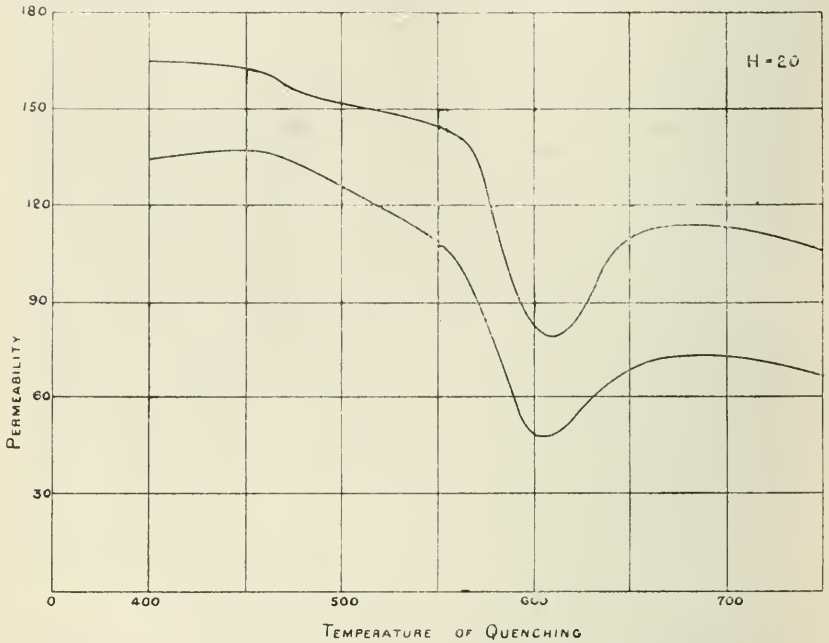


FIG. 2.—Variation of Permeability with Quenching Temperature.

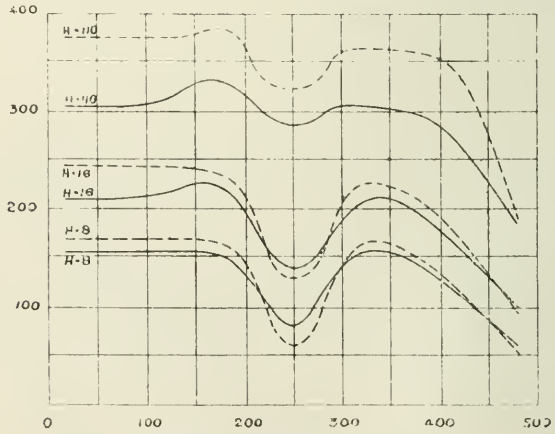


FIG. 3.—Effect of Baking Alloy No. 22.

and the dotted curves to tests at — 190° C. It will be seen that there is (*a*) an improvement effected by baking at 170° C., (*b*) a pronounced deterioration after baking at 250° C., and (*c*) a reversal of the liquid air effect for low fields after baking at temperatures ranging from 220° to 280° C.

With regard to the binary alloys of manganese and antimony and of manganese and boron, it may be said that the former group are the more magnetic. Of that series a maximum permeability was found in an alloy approximating to the composition indicated by the formula Mn_3Sb_2. An Mn_2Sb alloy was less permeable, more retentive, and exhibited much greater coercive force. An alloy containing about equal atomic proportions of manganese and boron was of similar quality to the Mn_2Sb alloy, both as regards induced magnetism and hysteresis.

The other binary alloys examined were only very feebly magnetic. Instead, therefore, of being tested in the same way as the foregoing alloys, they were magnetised in the narrow pole-gap of a powerful electromagnet. The most important facts ascertained were that the copper-manganese alloys were more retentive after quenching than in the condition as cast, whereas an alloy of 12·5 per cent. aluminium and 87·5 per cent. copper deteriorated on quenching and gave an improvement when cooled to liquid air temperature very similar to that found in the most magnetic copper-manganese-aluminium alloys when they had been subjected to like thermal treatment.* This similarity was so marked that the author in March, 1907, was led to the conclusion that the intermetallic compound Cu_3Al present in the aluminium-copper alloy must play an important part in the magnetism of the Heusler alloys. Further tests resulted in a hypothesis being published in February, 1909, that the magnetism of the Heusler alloys was due to the presence of solid solutions containing as a constituent the compound Cu_3Al. Shortly afterwards Heusler and Richarz published a paper † with data regarding a large number of these Heusler bronzes. When the permeability was indicated on a ternary diagram of the copper-manganese-aluminium system, it was found that the most magnetic alloys lay approximately along the line joining the points corresponding to Cu_3Al and Mn_3Al. They therefore ascribed the magnetic properties to the occurrence of a series of ternary magnetic compounds having the general formula $Cu_xMn_yAl_z$, where x and y may have any of the values 0, 1, 2, 3, &c., and $x + y = 3z$. This theory seemed unsatisfactory to the author of the present paper, because (*a*) ternary intermetallic compounds are exceedingly rare; (*b*) no indications of ternary compounds were found in the part of the copper-manganese-aluminium system investigated by Rosenhain and Lantsberry; ‡ (*c*) unless there were an exceedingly large number of such compounds the alloys could not exhibit that gradual variation of quality with composition which has been found in them; and (*d*) it is unlikely that the liquid air and other effects on these compounds should be so markedly similar to those on Cu_3Al.

The author inclined rather to the view that as Cu_3Al and Mn_3Al were the most magnetic members of their respective binary series, the Heusler alloys consisted of solid solutions of varying concentration of these two constituents, and that the magnetic quality was to be ascribed to the occurrence of these solid solutions. There were two methods by which the presence of solid solutions in the alloys could be ascertained, viz., the method of examining microscopically a polished section of the metal, and the method of determination of cooling curves. Owing to the hardness and brittleness of the alloys the metallographic method was clearly beset with great practical difficulties, and the failure of other experimenters to obtain any trustworthy information from microscopic examination of the alloys § made it apparently advisable to

* A. D. Ross and R. C. Gray, *Zeitschr. f. anorg. Chem.*, lxiii., 349, 1909.

† F. Heusler and F. Richarz, *Zeitschr. f. anorg. Chem.*, lxi., 265, 1909.

‡ W. Rosenhain and F. Lantsberry, *Proc. Inst. Mech. Eng.*, 1910.

§ See papers in the *Proc. Roy. Soc. Canada*, 1908, and *Phys. Rev.*, xxxi., 252, 1910.

attempt first the thermal investigations. The method consists in heating up the alloys to above their melting-points and then allowing them to cool slowly while time readings are taken of their temperature. It is of course very desirable that the cooling of the furnace in which the metal is tested should take place at an approximately uniform rate and not at a widely varying rate, such as would obtain if the cooling were regulated only by radiation and conduction. The author accordingly employed a modification of his electric resistance furnace, the current in the platinum coil being regulated by a rheostat. Tests were made when a platinum, platinum-iridium thermojunction was inserted alone in the furnace, and in this way information was obtained as to the proper method of increasing the resistance in the electric circuit so as to give a practically uniform rate of cooling of the furnace. The metal was placed in the furnace and heated until completely melted. The current was then reduced according to the scheme which had been drawn up, and time readings were taken of the temperature of the cooling alloy. To avoid any lag of temperature of the thermojunction, no shield was employed, but the end of the junction was embedded in the metal under examination. As it was also proposed to look for transformations occurring below the solidus and accompanied by heat evolution, it was necessary to have a sensitive means of measuring the e.m.f. of the couple. Neither the ordinary millivoltmeter nor the direct use of a suspended coil galvanometer afforded the requisite accuracy, and so a potentiometer method was adopted—a method which eliminated error due to change of resistance with temperature of the wires of the thermojunction. The usual null method did not admit of sufficient rapidity of adjustment, and so a cell was used to compensate the greater part of the e.m.f., the small outstanding part being measured in the usual way on the scale of a highly sensitive d'Arsonval galvanometer. When cooling curves (θ plotted against t, or θ against $dt/d\theta$) were drawn, they were in every case found to be of the form characteristic of solid solutions. In the copper-manganese-aluminium alloy No. 22, a transformation point below the solidus was found at 615° C., corresponding with the critical point found in the quenching tests and shown in Fig. 2. A similar though generally less marked transformation point was observed in each of the copper-manganese-aluminium alloys tested. The case of the copper-manganese-tin alloys is more complex. There are apparently several transformation points in these, but they are indicated by only very small evolutions of heat. The results, too, in one or two cases were not altogether consistent, and their discussion will be held over until further data are available. It may, however, be stated that the occurrence of a series of transformations in the solid state fully explains the complexity found in the quenching tests and also the much greater importance of normalising and annealing in the case of those tin bronzes than in the corresponding aluminium bronzes. *

Recently the author has commenced the examination of the microstructure of the copper-manganese-aluminium alloys. Some alloys have been examined which have a low manganese content, but which just fall within the magnetic region of the ternary system. This was done to ascertain the influence of added manganese on the copper-aluminium alloys, which binary system has been fully studied.† An alloy with 12 per cent. aluminium and 3·8 per cent. manganese resembled the binary alloy of copper and

* A. D. Ross, *Journ. Inst. of Metals*, No. 2, iv., 77 and 79, 1910; *Journ. de Phys.*, 5, i. 117, 1911.

† H. Carpenter and C. A Edwards, *Proc. Inst. Mech. Eng.*, 1907, 57; B. E. Curry, *Journ. of Phys. Chem.*, xi., 425, 1907; A. Gwyer, *Zeitschr. f. anorg. Chem.*, lvii., 113, 1908.

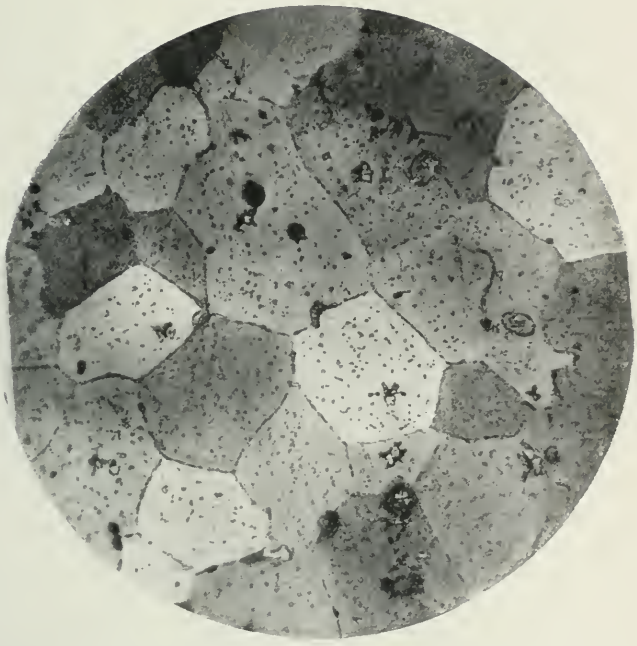


FIG. 4.—Microstructure of the Copper-manganese-aluminium Alloy, No. 22, in the condition as cast.

aluminium with the same percentage of aluminium. The effect of the added manganese was small, and only to be detected in a slightly increased amount of the dark-etching constituent. In an alloy with about the same relative proportions of copper and aluminium, but with double the manganese content, there was a pronounced change in structure. The lighter constituent has changed from intrusive acicular crystals to oval-shaped masses surrounded by the dark-etching constituent as a matrix. The grains, as seen in the microscope, appear to be shaded in the manner which is characteristic of a solid solution which is not homogeneous, but which contains layers of varying concentration. Fig. 4 shows a section of the highly magnetic copper-manganese-aluminium alloy No. 22. The ferric chloride etching reveals very clearly the polygonal grains of the solid solution. There are also a number of small crystals—of a fine blue tint when, seen under the microscope after etching—which will be observed scattered here and there throughout the section. The irregular round spots in the photograph are due to minute gas pores in the casting. As far as can be determined, the blue crystals are probably a binary alloy of manganese and aluminium, and they occur to a less extent in copper rich alloys. When alloy No. 22 is annealed at 180° C., so as to bring it into its best magnetic condition, the amount of this blue constituent is reduced; it is apparently a metastable phase produced by the cooling in the sand castings being too rapid to permit of the equilibrium condition corresponding with moderately low temperatures being at all perfectly attained.

McTaggart and Robertson * have suggested that the magnetic properties of the Heusler alloys are to be ascribed to the occurrence of manganese in a peculiar crystalline form when dissolved in copper and aluminium. A somewhat similar explanation has also been suggested more recently by Rhead,† and based on metallographic tests carried out solely on binary alloys. The author's investigations are in direct opposition to this hypothesis. None of the micrographs which have been prepared show any crystals of free manganese. The crystals shown in the drawings of McTaggart and Robertson seem to be due to imperfect alloying of the metallic elements, and the fact that the crystals diminished on annealing shows that the metal was not in a proper equilibrium condition. Possibly the crystals may be similar to the blue manganese-aluminium constituent referred to above, which is certainly not a strongly magnetic phase. The author also differs from Rhead in his view that the magnetism of the binary manganese alloys is due to such an allotropic crystalline and magnetic condition of manganese. Investigations on manganese-antimony,‡ manganese-tin,§ and manganese-aluminium || alloys would appear to have made it perfectly certain that the magnetic properties of these three series attain a maximum in each case corresponding with the occurrence of a definite intermetallic compound, and the amount of magnetism exhibited by any member of such a series depends solely on the magnetic binary compound present and its percentage amount.

The present investigations have shown that the magnetic properties of the copper-manganese-aluminium alloys are associated with the occurrence of solid solutions of varying concentration. These solid solutions, too, are very probably composed of the two intermetallic compounds Cu_3Al and Mn_3Al. Why the entrance of these feebly magnetic compounds into solid solutions

* H. A. McTaggart and J. K. Robertson, *Proc. Roy. Soc. Canada*, 3, ii., 31, 1908.
† E. L. Rhead, *Journ. Inst. of Metals*, 2, iv., 89, 1910.
‡ R. S. Williams, *Zeitschr. f. anorg. Chem.*, lv., 1, 1907.
§ R. S. Williams, *ibid.*
|| G. Hindricks, *Zeitschr. f. anorg. Chem.*, lix., 414, 1908.

should result in such an enormous increase in permeability is a problem of great interest and importance. One could readily understand why a solid solution of a magnetic metal A in a non-magnetic metal B might be much more magnetic than one would anticipate from the percentage amount of A present, for the magnetic quality will depend on the interactions between the magnetic "molecules" of A. If these molecules are separated from one another by B, which holds them in solution, the intermolecular forces which resist the magnetic polarising of the molecules in the case of pure A may be greatly diminished. A smaller magnetising force may thus give the same intensity of magnetisation in the metal. The case of a solid solution of two magnetic phases is more complicated, as the problem involves not only the intermolecular forces between like but also between unlike elementary magnets.

The researches summarised in this paper have been carried out in the Natural Philosophy Institute of the University of Glasgow, and a grant from the Carnegie Trust for the Universities of Scotland has met a considerable part of the expense incurred in the work.

THE HEUSLER ALLOYS.

Dr. A. A. Knowlton (University of Utah, U.S.A.) and **Dr. O. C. Clifford** (University of Utah, U.S.A.) also communicated a Paper on "The Heusler Alloys."

Although the relation of the magnetic properties of these alloys to the three factors, composition, thoroughness of mixing while in the molten state, and thermal treatment, has been one of the topics treated by nearly every investigator who has worked with these alloys ; and in spite of the extensive and valuable results contained in the original papers by Heusler and his co-workers (1), and in subsequent researches by Take (2), Asteroth (3), and others, there are certain fundamental questions to which it does not appear

TABLE I.

No.	Cu.	Mn.	Al.	History.
1	67·8	27·8	4·4	Cast from scrap from many previous specimens. Materials have been often cast and re-melted. Chilled from 250°.
3	63·8	27·5	8·7	New mixture. Annealed to room temperature.
4	63·3	26·4	10·3	Cast from scrap. Chilled from dull red heat.
5	63·3	26·4	10·3	From same melt as No. 4, but annealed to room temperature.
6	68·0	28·0	4·0	New mixture. Annealed to room temperature.
7	63·3	29·5	7·2	Al added to No. 6, remelted and chilled from 200 .
8	60·3	25·4	14·3	Al added to No. 7, remelted and chilled from 250°.
9	60·2	26·7	13·1	Remelted from scrap. Chilled from 200°.

that really satisfactory answers can yet be given. These questions may be stated as follows :—

1. What conditions of preparation and thermal treatment must be observed in order that an alloy of any given composition may be in condition to exhibit the maximum possible intensity of magnetisation when saturated ?

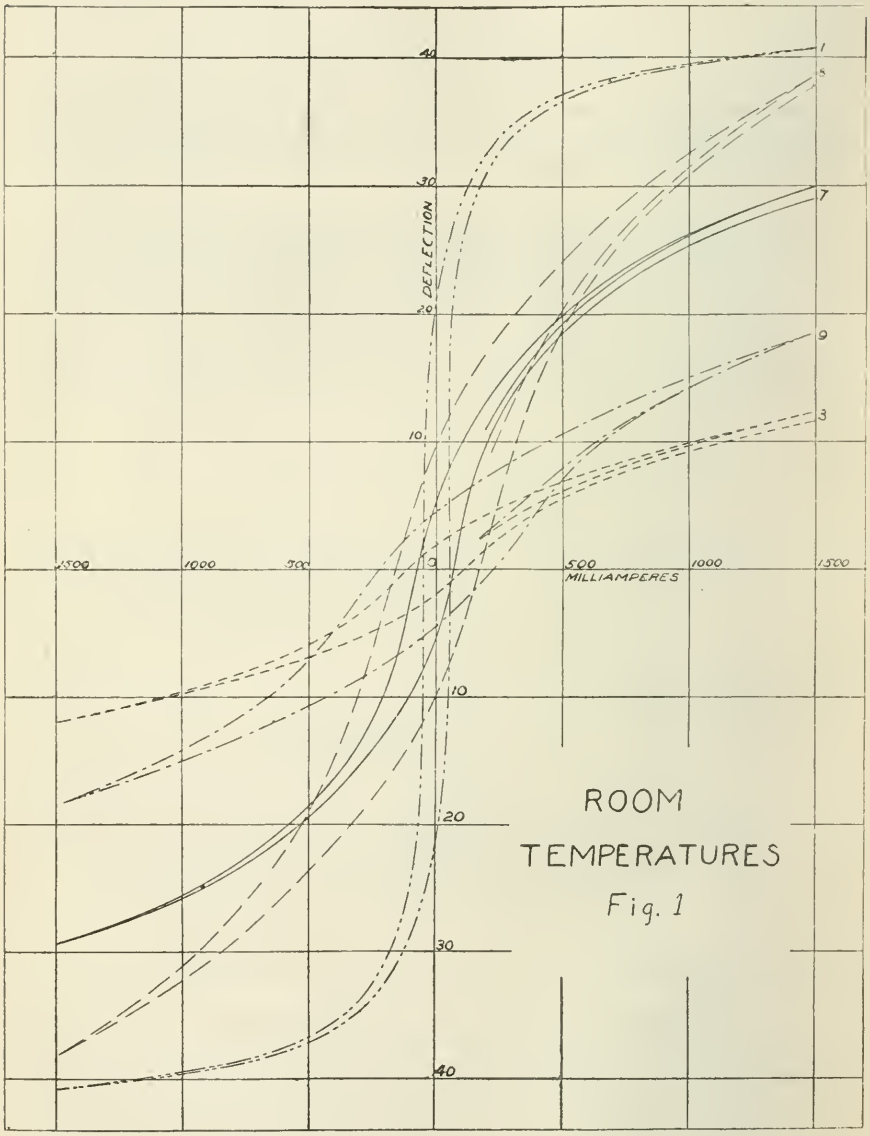
2. What are the exact relations between composition and the two factors of magnetic quality—hardness, and intensity of magnetisation at saturation ?

3. Upon what factors does the transformation point of a given alloy depend, and what is the exact form of the relation ?

The present paper is an account of some experiments which were undertaken as a further contribution to the study of these problems since the variables involved are so many and the relations so complex that it is only by the careful determination of the behaviour of many specimens in the hands of

different observers that we shall be likely to arrive at answers sufficiently definite to serve as criteria by which to test the various hypotheses as to the nature of the magnetic units in these alloys.

The specimens tested were in the form of rings, having the following



dimensions: Mean radius, 3·71 cm.; radial thickness, 0·6 cm.; width, 1·2 cm.; and wound with a primary of 864 turns and a secondary of 100 turns of No. 22 wire. The rings were prepared by prolonged heating in a graphite crucible, and cast in a hot carbon mould, as described in a previous paper (4). It was the original intention to prepare a series of alloys with increasing

aluminium content, and to cast three rings of each composition, one of which should be chilled from a high temperature, one cooled slowly to about 250° C. before chilling, and the third cooled slowly to room temperature, but the mechanical quality of all rings chilled from high temperatures was so poor that they generally broke in the process of grinding, so that although they often appeared to be strongly magnetic, no measurements could be made. On the other hand, all rings which were allowed to cool slowly to room temperature were of good mechanical but poor magnetic quality. Thus for one reason or another all the rings cast were rejected with the exception of the seven concerning which data is given in Table I.

Besides the Cu, Mn, Al, the rings contained a trace of iron and small but varying amounts of silicon which probably did not exceed 1 per cent. in any case.

The magnetic tests were made by the step-by-step method, the resistance coils used in varying the current being wound to give equal steps at 100°. The field due to the primary was 46·5 c.g.s. units per ampere and calibration of the galvanometer by means of a wooden ring of the same dimensions and winding showed that 1 cm. deflection indicated a change of 69 lines in the flux. As we are interested in changes rather than in absolute values, currents and galvanometer throws have been used as co-ordinates in our magnetisation curves.

Fig. 1 gives the hysteresis curves for Nos. 1, 3, 7, 8, and 9 six months after casting. Data were also taken on 5 and 6, but these resemble No. 9 so closely

Table II.

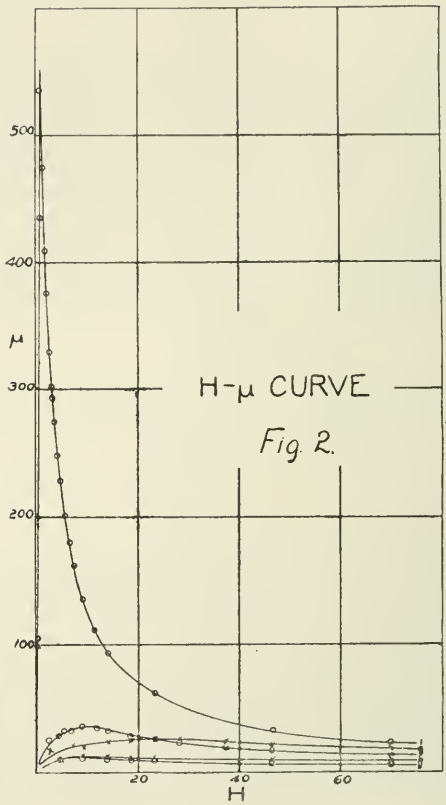
	1.	7.	9.	8.
Per cent Al.	4·4	7·2	13·1	14·3
H for max. μ	0·9	9·3	27·3	28·0

in their magnetic properties that the curves were not plotted. Perhaps the comparative softness of No. 1 is the most interesting feature of these curves. It is instructive to compare these curves with those in Fig. 3, which show the changes produced in No. 1 by heat treatment. The comparative importance of composition and thermal history is strikingly shown by these two figures.

Since it was not possible to bring the specimens to an absolutely neutral condition by the method of reversals used the curves as actually observed would have been slightly unsymmetrical with respect to the X axis. In order to make the comparison of different curves easier, this asymmetry has been overcome by using as ordinates the mean values of the summation of the throws to right and left with equal currents. In the original plot, made on 30 × 40 cm. section paper, the individual points fell, in most cases, within the width of the line drawn.

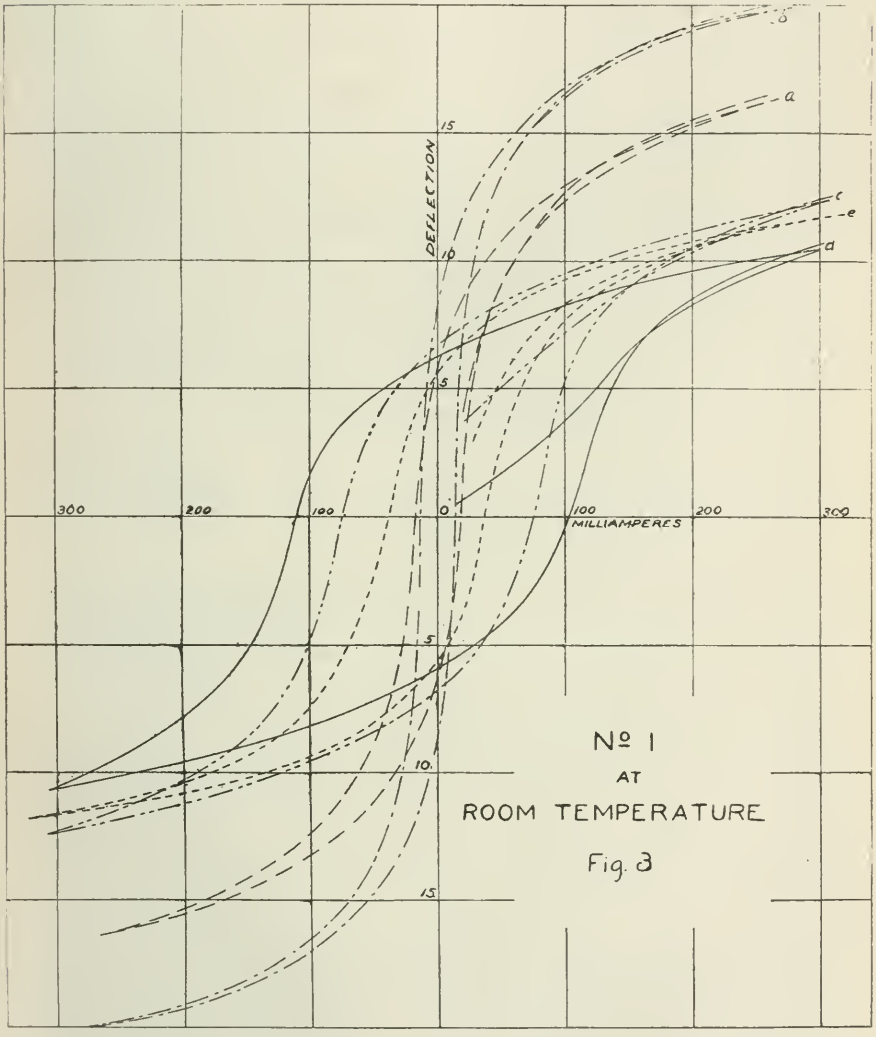
The H-μ curves (Fig. 2) were worked out from the data used in Fig. 1. If No. 3 be omitted the remaining specimens were prepared in essentially the same manner, and it would seem that the differences in the field corresponding to maximum permeability must be, for these four specimens, under the given conditions, a function of the composition. The data are insufficient to determine the precise nature of this relation further than that the maximum of the curves occurs for values of H which increase rapidly with increase in the percentage of aluminium, as is shown in the accompanying table (Table II.).

A comparison of these results with one another makes it strikingly evident that percentage composition plays a relatively unimportant part in determining the magnetic quality as compared with the effect of heat treatment. Nos. 1 and 6, for example, are of almost exactly the same composition but bear no resemblance to one another in quality. Unfortunately the history has been different in two respects—thoroughness of mixing, and method of cooling—so that it is not possible to determine from these specimens alone the part played by each. No. 1 was made from scrap, every part of which had been repeatedly remelted and cast, and probably represents as perfect a mixture as can be obtained, and was chilled from well above its transformation range.



No. 6, on the other hand, was a new mixture two or three times remelted and cast, and was chilled from a temperature slightly below its transformation point. It is, of course, impossible to separate the effects due to these two causes with certainty. We are, however, inclined to believe that the very great sensibility to heat treatment found in No. 1 was due to the perfection of mixture while the magnetic qualities as shown in Fig. 1 were due to the thermal treatment. The low induction of No. 6 is probably due to its having been cooled slowly through the lower part of its transformation range, as has been shown by Asteroth (5), and this injurious effect of annealing at the lower limit of transformation accounts also for the low maximum induction of No. 9 as compared with No. 8, which is of nearly the same composition. In both

cases the history shows treatment which must have ensured a good mixing, and the only difference is in the temperature of chilling. It may then be stated that No. 9 resembles No. 6 because it had been annealed through the lower limit of its transformation range (about 200°), and was therefore in nearly the same condition as it would have reached if cooled slowly to room temperature. No. 7, containing only one-half as high a percentage as



aluminium and with the same history as No. 9, is intermediate between No. 8 and No. 9. Here the explanation is that the lower limit of transformation for No. 7 is at 185°, hence it was not annealed through the injurious range although quenched at the same temperature as No. 9. This illustrates very strikingly the necessity of being sure that each specimen has been given the treatment required to bring it to its own best condition before exact conclusions can be drawn as to the effect of composition. The maximum

induction possible under the best conditions of mixing and chilling must depend upon the composition. It is undoubtedly true that under these conditions the maximum possible induction, for a given manganese content, increases with increasing percentage of aluminum, but there is no evidence which the writers would regard as conclusive as to precisely what composition would give the best results, although it has been assumed from the work of Heusler and Starck (*loc. cit.*) that this point was reached when atomic proportions were used.

The effects produced by thermal treatment have been extensively studied by Gumlich (4), Take (5), Hill (6), Asteroth (7), and Knowlton (8). Our results are in general in good accord with those previously obtained, but are in some particulars more detailed. The heater used was an oil bath with motor-driven stirrer. With one exception the curves given refer to ring No. 1, which showed an unusually high degree of sensitiveness to heat effects. During these experiments the specimen was wound with a secondary of only 50 turns, making the factor to be used in computing the induction from these curves 138 lines per centimetre of deflection.

A comparison with Fig. 1 shows that the induction curves of this particularly sensitive specimen taken after the various heat cycles differ more widely from one another in both saturation value and hardness than do the curves of Fig. 1, which refer to specimens of widely different composition. The curves as lettered represent the following conditions :—

(*a*) Original curve taken about six months after casting.

(*b*) After heating slowly to 120°, annealing for nine hours at that temperature and cooling slowly.

(*c*) After heating to 170°, annealing several hours and cooling slowly.

(*d*) After heating to 223°, cooling slowly.

(*e*) After heating to 250° and chilling.

It is to be regretted that the field was not pushed up in each case to the point of magnetic saturation. The procedure during these tests was to place the ring in the oil bath at room temperature and take data for a complete B and H curve, after which the temperature was raised at a fairly uniform rate of about one-half degree per minute. During this heating the magnetic quality was tested at frequent intervals, using a constant field strength of 69·8 units, and many complete induction curves were taken. Whenever the magnetic qualities showed signs of any irregular change the temperature was kept constant for so long a time as was necessary to carry that change to practical completion. During the first cycle there was a rapid loss of magnetic quality which continued at a fairly uniform rate up to about 120°, at which temperature the deflection had fallen from 20 cm. to about 5 cm. and the retentivity and coercive force were practically zero, as shown by the lower curve of Fig. 4. At this temperature the deflections began to increase with great rapidity, as is shown by the failure of the curve to close, so the temperature was kept constant and observations continued for about nine hours, during which time the change went on at a decreasing rate as shown. The increase in maximum induction is here accompanied by a slight increase in hardness. When this change was apparently complete the ring was allowed to cool slowly in the bath, and curve *b* of Fig. 3 was taken. Here we have, of course, been watching the progress of the familiar improvement produced by annealing just above 100°, which was first pointed out by Gumlich. It has also been shown that annealing at such temperatures profoundly affects the crystalline structure. Take found that in some of his specimens the transformation temperature was raised by successive heat cycles. We have never found this to be the case, and have, in fact, come to

look upon the transformation temperature as being the only really constant thing connected with these alloys. The observations here recorded would appear to explain this discrepancy in a simple manner. Evidently 120° is a critical point for this specimen, but the transformation results if allowed to go to completion in the formation of a more strongly magnetic material. It appears probable that Take's specimens were cooled before the reconstruction of the elementary magnets had time to progress very far. During the second cycle the deflection decreased less rapidly with temperature, and there was no further change at 120°, although the temperature was kept constant at that

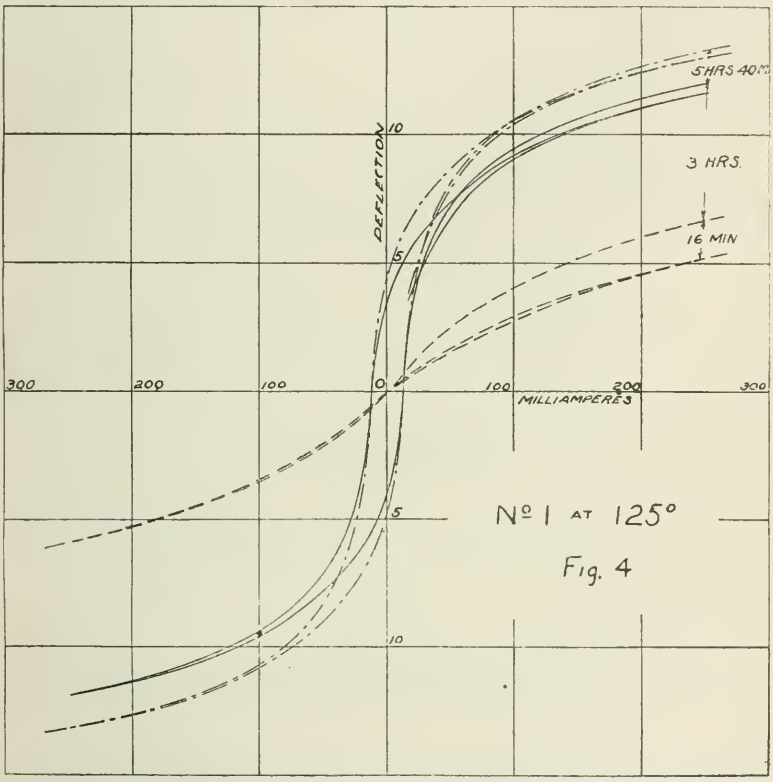


Fig. 4

point for some time : but at 170° a second increase began which was, however, much smaller than at 120° and was complete in a much shorter time. Slow cooling to room temperature left the ring in the magnetic condition shown in curve *c* of Fig. 3. The injurious effect of annealing at about this temperature has been previously pointed out, and it has been shown that the changes in crystalline structure at this point are in the opposite direction to those at just above 100°. A third cycle showed no change at either 120° or 170°, and resulted in complete loss of magnetic quality at 223°, with no recovery on prolonged heating at this temperature, which is then the critical temperature. The enormous increase in hardness and general deterioration in magnetic quality shown in *d*, Fig. 3, is probably due more to the slow cooling which followed than to the annealing at 220°.

Fig. 5 shows the effect produced by chilling from various temperatures. It will be noted that there is a considerable improvement in quality, which would appear to be a maximum for chilling from a temperature of slightly below 250°. After this treatment a second complete cycle was carried out, and it was found that the specimen had been so far restored to its original condition that the changes at 120° and 170° occurred as in the first cycle. The complete temperature magnetisation curve for this cycle is given in Fig. 6.

Fig. 7 shows the change in the deflection with time during the second cycle. The dotted line represents the deflection caused by the constant flux due to the applied field, and the height of the curve above this line is proportional to the intensity of magnetisation. It has been found that this curve referred

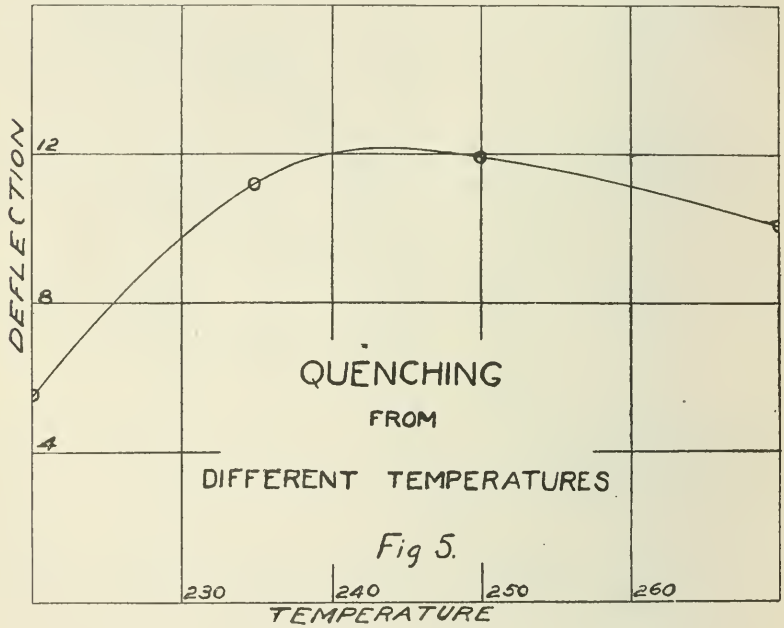


Fig 5.

to the dotted line as an axis is very accurately represented by an equation of the form $I = I(1 - e^{-kt})$. In chemical work an equation of this form for the velocity of a reaction indicates a monomolecular change. If a like interpretation is allowable here, this curve must mean that the sudden increase in the magnetic quality was the result of some rearrangement of the molecules within previously existing groups, and that it was not brought about by the formation of new groups. Similar changes were found with other specimens, but the first change did not always occur at the same temperature in different specimens. In No. 7, for example, the first change began at 140° instead of 120°. It seems likely that this is due to the hardness of No. 7 as compared with No. 1.

Early in our experiments with the very soft No. 1 it was found that upon removing the magnetising field a sharp click was emitted, which was comparable in intensity with the sound of a weakly excited telegraph instrument, although the ring itself was wound with several layers of insulated wire and

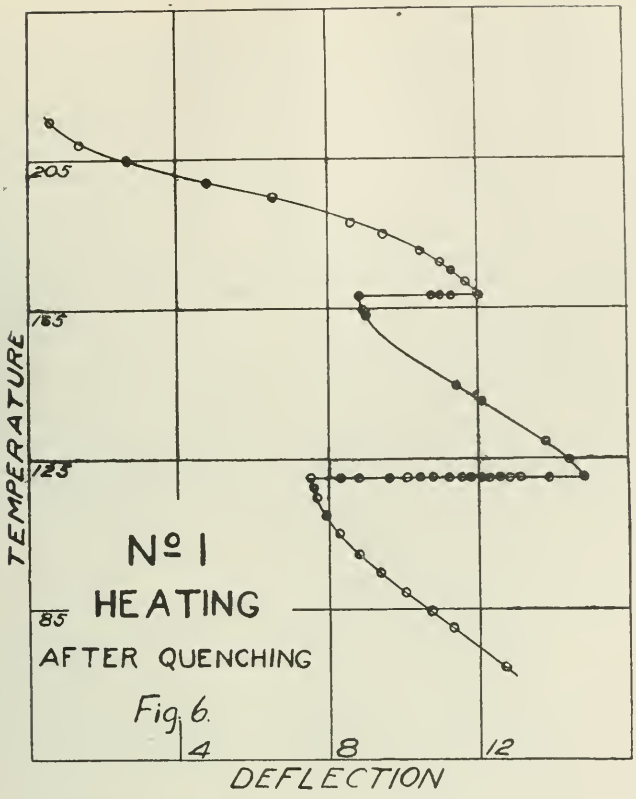

205
163
123
85
TEMPERATURE
Nº 1
HEATING
AFTER QUENCHING
4
8
12
DEFLECTION

Fig. 6.

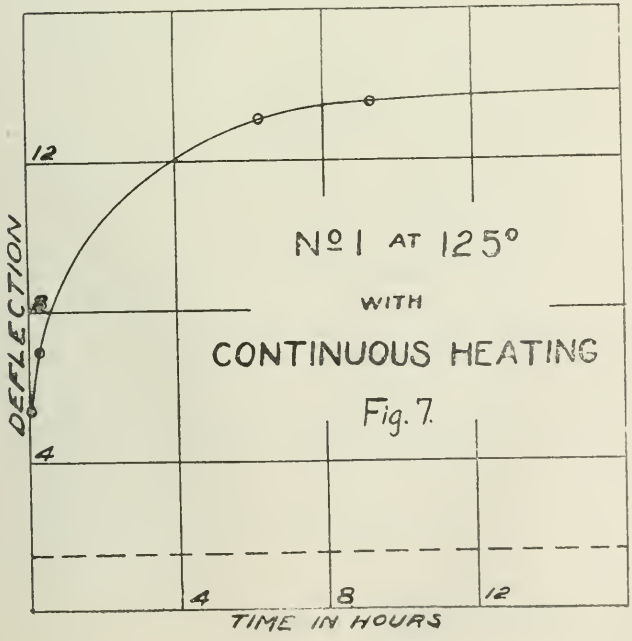

12
8
4
DEFLECTION
Nº 1 AT 125°
WITH
CONTINUOUS HEATING
4
8
12
TIME IN HOURS

Fig. 7.

the whole thickly covered with insulating tape. This sound was always produced on demagnetisation, but its intensity was very greatly diminished by any heat treatment, which increased the magnetic hardness and restored by treatments having the opposite effect. Investigation proved that this effect was also present in all our other rings, as well as in a number of rods which had been used in previous experiments, but in no other case was it as pronounced as in No. 1. A similar but much feebler effect is, of course, well known in iron. In iron also any change in magnetisation is accompanied by the production of sound, while here no effect was ever observed at the time of making the field, a result which may point to a high magnetic viscosity.

From the evidence presented, it appears that, in spite of the work heretofore done, we do not know what proportions will give us the alloy of maximum possible magnetisation, and that it will probably be impossible to decide this definitely until the conditions of thermal treatment necessary to put particular specimens in their best condition have been worked out over a wide range of composition. A systematic study of these conditions is planned for the near future. It appears that sensitiveness to heat treatment and magnetic hardness are closely dependent upon the proportion of aluminium present, while the transformation temperatures depend largely upon the percentage of copper, but that these are not the only effective factors. Here again further work is needed with specimens carefully treated to bring out the best possible characteristics of each composition.

The fact that the audible effect is diminished by any treatment which increases the magnetic hardness appears to favour the supposition that the resistances causing hysteresis loss are in part at least mechanical and dependent upon the nature of the matrix which incloses the magnetic group. If this be true, it becomes a matter of importance to determine which changes are due to changes in the matrix (hardness) and which are due to changes in the magnetic unit itself, and for this purpose extensive determinations of the behaviour in intense fields are needed.

There seem to be three possible hypothesis as to the nature of the magnetic units in these alloys, which may be stated as follows :—

1. The magnetic units are the molecules of a chemical compound of manganese and aluminium, or groups of such molecules.

2. The magnetic units consist of manganese molecules or of groups of such molecules.

3. The magnetic units are complex groups, which form the structural elements of a certain type of mixed crystal, and contain at least two different kinds of chemical molecules.

The hypothesis of a chemical compound is perhaps the simplest, and receives strong support by analogy, since E. Wedekind (9) has shown that nearly all of the trivalent elements of the boron and nitrogen groups form strongly ferromagnetic compounds with manganese. The direct evidence, however, appears to indicate that the alloys consist of a series of solid solutions,* while it does not seem easy to account for the extreme variability of the alloys if their properties are those of a definite compound. In particular it would be expected that the transformation temperature would be the same for all specimens if the magnetic units were the same in all.

The second hypothesis which is, of course, the allotropic theory as applied to these alloys, is well stated in an abstract † of C. E. Guilhaume's article on the "Theory of the Heusler Alloys."‡ "It seems that Al and Sn possess the

* L. Guillet, Soc. d'Encouragement, *Rev. de met. Mem.*, pp. 87–111, July 1, 1906.
† *Science Abstracts*, 1905–1907.
‡ *Ind. Elect.*, 14, pp. 533–536, December, 1905.

property of raising, in certain cases, the transformation temperatures of the metals with which they are combined, whether these transformations are characterised by the passage from the crystalline to the amorphous state (fusion) or to another crystalline state which possesses magnetic properties." The chief objection to this hypothesis upon experimental grounds seems to be that it assumes a strongly ferromagnetic state for manganese at low temperatures. P. Weiss and H. K. Onnes (10) have carried out experiments as low as 14° abs. with no indication of such a state, but find, on the contrary, that manganese freed from its oxides by prolonged heating in a stream of hydrogen is weakly ferromagnetic at ordinary temperatures, so that the effect of the aluminium would seem to be to increase the moment of the magnetic units rather than to change the temperature at which they come into existence.

The third hypothesis has much in common with the second as we understand it, but avoids the assumption of strongly ferromagnetic manganese by regarding the magnet units as complex molecular groups which form one of the structural elements of certain crystals which have been found to be present in all magnetic specimens, and to change with any heat treatment which affects the magnetic properties.* Upon this hypothesis the changes observed in No. 1 would be interpreted somewhat as follows :—

The specimen as prepared contained a certain number of elementary magnets, each consisting of a group of molecules of at least two kinds, which may be thought of as either arranged in definite positions with respect to one another (like the atomic arrangements of stereo chemistry) or as moving in well-defined orbits within the group, the magnetic moment of each group being in some way determined by this arrangement or motion. The gradual loss of magnetic quality with rising temperature would then be explained as the result of thermal agitation in which the group takes part as a whole in accordance with the kinetic hypothesis precisely as in the case of a pure ferromagnetic metal. The increase in intensity of magnetisation at 120° must, on the other hand, be due to structural changes which might conceivably be : (*a*) an increase in the magnetic moment of each group consequent upon a change to an arrangement of greater stability ; (*b*) an increase in the number of groups ; (*c*) a softening which allows the field to exert its influence more effectively. The third possibility may be rejected at once since the induction curves taken during the progress of the change show an increase in hardness rather than a decrease. On cooling to room temperature the new arrangements or new groups persist, as is shown by the fact that no change occurred at 120° on the second heating. It is in fact certain that a change similar to that which took place at 120° goes on slowly at ordinary temperatures, thus indicating that the state reached by annealing is the stable one. It will be remembered also that the change in hardness was in this case slight.

At 170° a second rearrangement results in the formation of groups of still greater stability, and at this point also the matrix undergoes a change which results in an enormous increase in hardness after cooling. At 223° the specimen has become non-magnetic because of the thermal agitation, and above this temperature the groups change back to the form stable at 250°, which is preserved on chilling, and the specimen therefore repeats the changes as found.

* *Phys. Rev.*, January, 1911.

Notes and References.

1. *Deutsch. Phys. Gesell. Verh.*, **5**, 12, pp. 219–234, June 30, 1903.
2. Ibid., **7**, 7, pp. 133–145, April 15, 1905.
3. Ibid., **10**, 2, pp. 21–32, January 30, 1908.
4. *Ann. de Physik.*, **16**, 3, pp. 535–550, March 14, 1905.
5. *Loc. cit.*
6. *Phys. Rev.*, **21**, pp. 335–342, November, 1905.
7. *Loc. cit.*
8. *Phys. Rev.*, **22**, 1, pp. 54–68, January, 1911.
9. *Deutsch. Phys. Gesell. Verh.*, **8**, 20, pp. 412–416, October, 1906.
10. *Comptes Rendus*, **150**, pp. 687–689, March 14, 1910.

The University of Utah.
March 1, 1912.

THE MAGNETIC PROPERTIES OF COMPOUNDS OF MANGANESE WITH PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH.

A Note by **Dr. S. Hilpert**, **Dr. T. Dieckmann**, and **Dr. E. Colver-Glauert** on "The Magnetic Properties of Compounds of Manganese with Phosphorus, Arsenic, Antimony, and Bismuth" was read by Dr. Colver-Glauert.

This paper only deals shortly with magnetic properties which were discovered during a chemical research on the manganese compounds.

In examining these compounds with a view to discovering a connection between magnetic properties and chemical combinations, the greatest difficulty is to know whether a compound or only a mechanical mixture is being worked upon. It was possible, working with arsenic vapour at high temperature and with high pressure, to produce the pure compound MnAs, and to prove it to be a chemical compound. By heating this compound in a stream of hydrogen, arsenic can be distilled away, so that a series of products can be produced containing different percentages of arsenic. The magnetic examination of this series proves that the compound itself is by far the most strongly magnetic, and as the percentage of arsenic falls, so does the magnetisability.

Such manganese compounds as have already been magnetically examined also showed that the temperature of the magnetic change point was most strongly dependent upon the previous treatment.

As the pure chemical compounds used for this research were examined, namely MnBi, MnSb, MnAs, MnP, the magnetic change point was found to be higher or lower in proportion to the atomic weights :—

	Magnetic Change Point.
MnBi ...	... 360°–380°
MnSb ...	... 310°–320°
MnAs ...	... 45°–50°
MnP ...	... 18°–25°

The properties of the MnP are very suitable for demonstration, since the change point occurs at such a low temperature. If warmed in the hand it is unmagnetic and becomes magnetic again as soon as it is placed in cooled water.

This experiment was demonstrated in the optical lantern.

NOTE UPON THE MAGNETIC AND NON-MAGNETIC QUALITIES OF IRON ALLOYS.

The following contribution to the Discussion by the **Chairman, Sir Robert Hadfield, F.R.S.**, was laid before the meeting.

Most of my present remarks originate from those in connection with the interesting paper by Mr. McCance on "The Constitution of Troostite and the Tempering of Steel," read before the Institution of Mechanical Engineers in December, 1910. I see no reason to modify the statements then made, and seeing that they deal with a question which is of interest to this Society at the present time, namely, regarding magnetic and non-magnetic qualities of special alloys of iron and steel, I have extracted somewhat freely from this contribution to the discussion in question.

"β Iron is known to be Non-magnetic."

This quotation from the discussion mentioned will form my text, not that I agree with the statement—in fact I disagree—but because it represents the considerations mainly dealt with in the following remarks.

"It was doubtful whether any definite facts were yet available that β iron really existed, and the fact that iron was non-magnetic beyond certain temperatures could hardly be claimed as proof of allotropic modifications, and still less as a proof of the existence of an adamantine β form of iron which the expression 'β iron' really implied.

"Moreover, surely the changes produced in molecular constitution were not those coming at all under the head of allotropy, using the term in its original meaning, because all matter was more or less subject to changes in molecular constitution by temperature variations, yet one did not speak of these as allotropic modifications. Therefore, the fact that iron became non-magnetic by heating would hardly seem to be any real proof of the existence of an allotropic β form, any more than the fact that the iron present in manganese steel, which was practically non-magnetic at ordinary temperatures, owed its non-magnetic qualities to the so-called β form of iron. This latter point was specially important, because manganese steel, being very hard under the tool, could not be machined, but was absolutely different in its hardness as compared with hardened carbon-steel. The Brinell ball hardness number of manganese steel was only about 200, whereas that of ordinary carbon steel hardened varied from 700 to 850.

"Whilst above a point in temperature which might be termed for convenience 'B'—which must not, however, be taken to have the same significance as the term 'Beta' as hitherto employed—there was a modification in what might be termed the molecular constitution of iron; this also occurred below this point 'B.' Iron, like many other metals, showed considerable difference in its molecular constitution with the rise or fall of temperature. In other words, its condition was not stable any more than other bodies. The use of terms 'A' and 'B,' as they did not carry a 'biassed significance,' as designating some differences, would therefore be much more satisfactory until facts were proved to the contrary, than the use of the terms 'α' and

'β' by the allotropists. That such forms of iron existed had not yet been proved.

"M. Grenet in his excellent paper* on 'La Transformation de l'Acier dans les Limites de Temperature' had adopted a similar way of describing the changes produced by variations in temperature. He termed them 'conditions of stability,' condition 'C' (or as above 'B') being the stability when cold, and condition 'H' (or as above 'A') the stability when hot. Moreover, he pointed out, when studying the iron and carbon alloys, that no 'distinction should be made between the changes in the condition of the iron and the dissolution of the iron into a solid solution, since both are one and the same thing.'

"It seemed to be commonly accepted that all our metallurgical friends in France were allotropists in the sense he understood Mr. McCance claimed. However, this was not so, as M. H. le Chatelier, whose long experience and great ability as a scientist in metallurgical as well as other matters was well known, had himself pointed out that, as time went on and facts accumulated, he was more and more convinced that the difference between so-called α and β iron was not a difference of allotropic state or condition, such as between γ iron and the stable varieties in the cold condition. M. Chatelier states: 'Je suis de plus en plus convaincu que la différence entre le fer α et le fer β n'est pas une différence d'état allotropique, comme entre le fer γ et les variétés stables à froid. Tous les corps magnétiques, sans aucune exception, présentent, à une certaine température, la même chute progressive des propriétés magnétiques. C'est un phénomène caractéristique des corps magnétiques et seulement de ceux-là.'

"Moreover, there were iron alloys now well known and in use which were more magnetic than iron itself. Under the allotropic theory would not this perforce mean still another allotropic form of iron?—if so it would appear to be untenable. Apparently this was the only explanation upon which the allotropist could fall back, that was, in view of his previous claims that the differences in the magnetic properties of iron alloys, including those which were non-magnetic, were owing to the particular form or condition of iron existing in them. When an alloy of iron was more magnetic than iron itself this would necessarily, so the writer thinks, demand another allotropic form of iron to explain this condition.

"As bearing on this question of allotropy, in which magnetic condition really played a considerable part, that is, according to the theories of the allotropist, Professor A. A. Knowlton, one of America's most able scientists in this matter, has pointed out in his paper,† in connection with various elements, that these varied in what he termed 'atomic susceptibility which bore no relation to the ordinary or mass susceptibility,' whilst 'ferromagnetism was undoubtedly neither atomic nor molecular, but crystalline.' Here was the statement in full with which he concluded his paper: 'Diamagnetism in all cases, except possibly bismuth and the Cu and Sn alloys of Clifford, is to be regarded as an atomic property, as is also paramagnetism in the narrower sense of the term, *while ferromagnetism is undoubtedly neither atomic nor molecular, but crystalline.* Indeed, it is questionable if the word "molecule" has in the present state of our knowledge any definite physical significance whatever when applied to the solid state. Is there any evidence for the so-called molecular theory which will not apply equally well to prove that magnetism is a crystalline property?'

* *Bulletin et Comptes Rendus Mensuels de la Société de l'Industrie Minérale*, August, 1910.

† "The Present State of Our Knowledge of Magnetic Materials," read before the Am. Assn. for the Advancement of Science, Boston, 1909.

"This threw out a new line of thought, which seemed to offer a more satisfactory conclusion than those hitherto advanced in this particular field of research.

"Professor B. Hopkinson, in his reply to the discussion which took place on the joint paper by him and the writer (Sir R. Hadfield) on 'The Magnetic Properties of Iron and its Alloys in Intense Fields,'* mentioned with reference to the critical point 750° C., at which point the magnetism of iron disappeared quite suddenly, that he considered this result was suggestive as to the nature of magnetism. His view was that it seemed probable that temperature had an effect on the molecular constitution, and it was a question whether reduced magnetism arose from the total destruction of the magnetism of certain molecules, or whether it arose from a gradual change taking place in all the molecules. The former was more probably the correct explanation. This showed that one could not generalise upon this question. We must have more light before pronouncing positively as to the peculiarities noticed in the behaviour of iron alloys.

"To sum up, we evidently wanted much more light as to *the molecular constitution of the metal* iron itself, or to use Professor Knowlton's term, 'to study the peculiar grouping of the ultimate particles or molecules, in the chemical sense,' of the metal iron, before we could make any further important advance in the direction desired by the electrical engineer. The problem would no doubt be solved, but to do this would also mean investigations probably on quite new lines of thought. As Professor Knowlton pointed out, the subject was already recognised to be of the greatest importance, seeing that *Science Abstracts* since 1900 contained references to more than 500 papers on the question of magnetic materials and their properties. Yet we were still very much in the dark on many important matters. It was here where the pure scientist could assist, and no doubt he would do this and come to our rescue."

* *Proceedings, Inst. of Civil Engineers*, December, 1910, p. 304.

DISCUSSION.

The subject was then thrown open for general discussion which, at the invitation of the Chairman, was opened by Professor H. du Bois (Berlin).

Professor H. du Bois : I am not prepared to offer any very coherent remarks, but I may be allowed to make a few comments. I have always thought that, from the physical standpoint of the magnetician, it would be useful to extend our knowledge about the magnetic properties of ferromagnetic substances generally. In 1900 I submitted to the first International Congress of Physicists in Paris a report on magnetic properties of matter, *alias* magneto-chemistry, in which I tried to summarise everything that was then known about substances other than the three classical metals. I also added the fourth metal, manganese, because then—that is to say, in 1900—certain experiments were known—amongst others those of Seckelson, of Heidelberg—which could be interpreted so as to lead to a saturation value of about 15 c.g.s. (specific magnetisation per gramme), which is rather strong, considering that for iron it is 217. As you will be aware, Professor P. Weiss has electrolytically prepared manganese which is ferromagnetic, and he has sent me a sample of it; it is quite easy to see that it really is ferromagnetic. In a conversation which I had with Professor Weiss in Paris he admitted that in the electrolytic preparation of the manganese the hydrogen may combine with the kathode, and, having such a low atomic weight, it is very difficult to show it chemically; so this question is not quite settled. In 1900 I think I submitted about all that was known about minerals, mostly in the natural state; then there were very few artificial compounds which had been studied and were understood. Amongst the minerals were Fe_3O_4, pyrrhotine, ilmenite, and some other ores considered by mineralogists as "attractive." From the physical point of view we must feel extremely grateful to chemists and metallurgists that they have furnished splendid new material, some of which has been shown to us here to-night. For the knowledge of magnetism and a deeper insight into its nature, I consider it to be of the very greatest importance, and I hope that chemists and metallurgists will go on unrelentingly in their efforts to provide us with such material. In return, if the magnetic balance which has been referred to to-night proves of any use, I hope those investigators will address remarks and criticisms about it to me, and we will do all we can to improve it and make it serve such scientific and practical purposes as may be desired.

In the second place I may, perhaps, state that we have made some experiments on some of the substances mentioned to-night, which have not yet been published, concerning the transition points which we have determined in a more accurate way. Some of the numbers formerly determined by Dr. Hilpert in a rough-and-ready way were found to differ from those derived by improved methods, which provisionally stand as follows:—

Magnetite	555°	Cupri-ferrite	418°
Cobalto-ferrite... ...	520°	Calcium-ferrite ...	156°

Of more interest is a reference to the magneto-optical researches made in my laboratory by Dr. Loria and Mr. Martin, which will be soon published. These were originally started by myself in 1889. A piece of manganese steel —one of the first made, I think—was kindly sent to me by our Chairman, and I may personally, even after the lapse of so many years, tender my thanks to

him for kindly giving me that sample. I found that that piece of manganese steel, which was non-ferromagnetic as a lump, distinctly showed the magneto-optical effect discovered by John Kerr, and which, as you know, consists in the rotation of the plane of polarisation of reflected light when the mirror is magnetised. This manganese steel showed the effect, but it was variable for different patches in the mirror which reflected the light. That is no wonder, for we have to-night seen many of these beautiful metallographical specimens projected, and most of them consist of a lot of patches of different composition beside one another. What may be called the ordinary macromagnetic methods, of course, give us the average of the lump of material, whereas in these cases we can study the behaviour of very small patches of something like a few millimetres extent. The light penetrates, if at all, for only a few millionths of a millimetre, so that the depth of penetration in these cases practically claims no part. In one way this magneto-optical method offers a method of studying the surface patch by patch; but on the other hand it is rather unsatisfactory, because the amount of labour necessary to work through a large piece of metal is enormous, and the method is not quite easy of adaptation. So I hardly believe it would be useful for obtaining further insight into the phenomenon. By analogy with those old experiments with manganese steel we have now also tried non-magnetic ferronickel, which was kindly given to us by Dr. Hilpert and Dr. Colver-Glauert. The 25 per cent. and 27 per cent. alloy was tried, which was also non-magnetic as a lump, and again we found the same effect as with manganese steel.

We have also tried compounds which are much better defined chemically as well as physically; we then have a perfectly homogeneous and uniform material; the surface also is uniform, and we can grind and polish mirrors on it, more satisfactory to work with. Most of these compounds—in so far as they are more or less strongly ferromagnetic—gave us the Kerr effect. In particular cupri-ferrite gave it; some of the other ferrites, such as calcium-ferrite and cobalt-ferrite, do not measurably show it; they are probably not sufficiently strongly ferromagnetic. We have tested bismuthite, antimonite, and stannite of manganese also, with a positive result; the arsenite and phosphite which Dr. Hilpert showed us just now were until the present only to be had in powdered form, and this evidently is not suitable for such experiments. They are not only interesting in so far as they show us further evidence of ferromagnetism, but also because of the unusual curves of dispersion they give; for instance, the sense of rotation is often different for different wave-lengths. And though it is hardly of metallographic interest, we here have the materials showing optical qualities which simple metals do not give us, as such curves of dispersion were hitherto unknown.

I would lastly mention something referring to what was said by Professor Wedekind on the subject of certain earths. In 1899 I had the good fortune to show that the salts of the rare earths were very much more strongly paramagnetic than those of the iron series of metals. Lately Professor Morris Owen, who worked in my laboratory, has found that metallic praseodymium, neodymium, and erbium had only a fraction of the specific susceptibility of oxygen; taking oxygen as 100 millionths, he found something between 20- and 50-millionths; they also follow Curie's law in the same roughly approximate way as oxygen.

Professor B. Hopkinson, F.R.S.: I do not think there is much that I can say on these very interesting Papers. They cover a great deal of ground, and I do not feel competent to discuss them in detail. But they have suggested one or two general reflections which perhaps I might mention. It strikes me, first of all, that we are here hearing of many different magnetic

materials. Many years ago it was supposed that the only magnetic materials were nickel, iron, and cobalt. But we have been introduced—personally I have for the first time to-night—to a considerable number of compounds which contain none of these metals, but which are nevertheless strongly magnetic. The Heusler alloys, which have been known for a number of years, are of course of this character, but it appears now that there are a large number of compounds of the same kind composed of a considerable variety of non-magnetic elements. I think a systematic study of these compounds may throw light in the course of time on the elusive phenomenon of magnetism, of which really we do not know much at present. It seems to me that the most promising lines on which to undertake such a study—and I see that to some extent those lines have been followed in the work before us—the most promising lines are first to make a test of magnetism in fields of very high density, the type of experiment which I was doing the other day, and in which I was associated with you, Sir. And the other line of investigation, I think, is the relation between the saturation value of magnetisation determined in that way and the temperature, a matter which was investigated some years ago for iron and other materials by Professor Curie. I have not at the moment got all the details of that work in my mind, but my recollection of Professor Curie's work is that he determined the relation between the saturation intensity of various materials and the temperature, and found that in each case it could be expressed by an equation which was of much the same form for the different materials, involving, I think, one or two constants. These constants varied from one material to another; but the general character of the relation seemed to be much the same as that obtaining between the pressure and the temperature of a gas or liquid which was near its critical point. That always seemed to me a very illuminating analogy, and I think it should be followed up. The best way of doing so, I think, is to study the relation between saturation intensity of magnetisation and the temperature. I think it is important to use a high field, because by the use of high fields accidental effects of the kind of structure which is revealed by the microscope, those effects on the magnetic properties which are very marked in fields of low density, are eliminated by having high fields. There was one experiment I tried, of which I gave the results in this theatre a year or two ago, in which I ascertained the effect on the intensity of magnetisation of pure iron of subjecting it to very high stress. It is well known that in fields of low density if you stress iron even within the elastic limit, you considerably affect its magnetic permeability. I took a short bar of iron and placed it between the poles of a powerful magnet, sufficiently powerful to produce a magnetic force of 5,000 or 6,000 units, and to magnetise the iron to saturation. It was arranged so that the two ends of the bar passed through the poles of the magnet, and they could be stretched by a screw, enabling one to put a big stress on to the little bar of iron. Means were then taken of measuring the magnetisation. I could put on an amount of stretch reaching the yield-point of the material and sufficient to cause the iron to "flow," without changing the intensity of magnetisation by so much as 1 per cent. Such treatment has no effect upon the intensity of magnetisation in very high fields. In one of the papers read to-night, I think that of Dr. Wedekind, some very interesting compounds of non-magnetic metals were described, and he proceeded to high fields. The diagram which he showed represents the relation of intensity of magnetisation to the magnetic force. The latter goes as high as 800. But even in that field it is apparent that such compounds as manganese-antimony and manganese-boride are still very far from saturation, and it seems probable that the

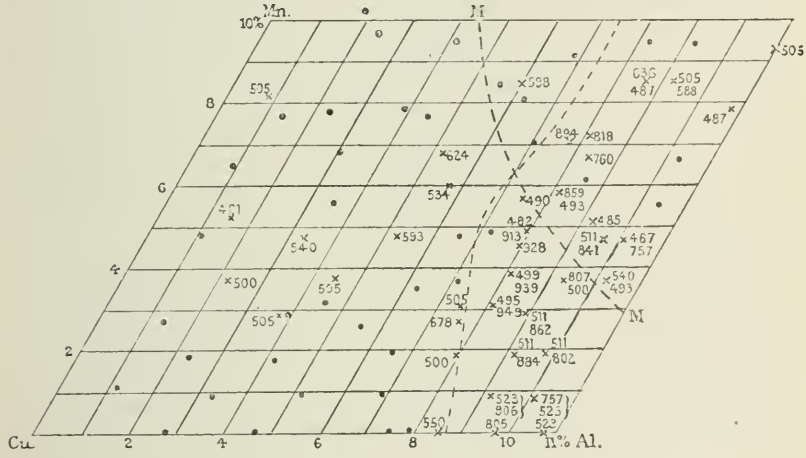
quantitative, though perhaps not the qualitative, relation between the magnetisation of those several compounds would be considerably altered if instead of a field of 800 we took a field of 8,000. I hope, therefore, that research on these points will be carried out in which the intensity of the magnetising field will be carried to a figure which produces complete saturation.

Dr. W. Rosenhain: The mass of papers which have been placed before us to-night require a good deal more study and understanding than it has been possible to bring to them in the time during which they have been in my hands, so that I cannot hope to discuss them in anything like a detailed way, or with the amount of information behind me which I should like to have. But there are one or two points which have been raised and which interest me particularly, and to which I should therefore like to refer. To take the last first, I would like to protest gently against Professor Hopkinson's suggestion that the effects of the micro-structure, the minute internal structure, are to be regarded as accidental. I quite see the point of his contention, namely, that in a field of high intensity one obtains a quantity or a series of quantities which are of more fundamental character. But I would remind him that these quantities are not the only things to be considered, and that by using these fields of high intensity he would obliterate the effects of many features which are of interest and importance in themselves. That brings me to the question of the connection between micro-structure and magnetic properties, and when we hear that the connection cannot be followed and accurately traced in complex alloys of iron, carbon, and nickel I am not surprised, and I do not think it is an imputation on the probability of any theory. As a matter of fact, we cannot correlate the magnetic properties with the micro-structure in such a simple body as practically pure iron. If one takes a scale of micro-structure in a series of transformer sheets, all of the same composition but mechanically and thermally differently treated, it is not possible to draw a direct inference from the micro-structure to the magnetic properties even in this simple case. And yet investigators seem to think they should find a close relation between them in complex alloys. I draw the inference particularly from the suggestions of Professor Hopkinson that very likely there are two sets of circumstances at work; one is of a purely molecular and the other of a structural character, and it seems to me that we shall have to try to disentangle those two. Very likely a combination of work at high intensity, which Professor Hopkinson favours, and work possibly at lower intensities may enable us to do something in that direction.

Sir Robert Hadfield tempted me in his opening remarks, for he referred to an adamantine form of Beta iron. I will only say now that although I believe in the existence of a hard form of Beta iron, I refuse to accept the term "adamantine." Some of us believe that there is a distinctly harder form of iron, which is stable at high temperatures, and further may be more or less retained by quenching, but it is not necessarily adamantine, it may be merely distinctly harder than the others. But that really is a side issue.

The other point I would refer to concerns the reference to my own work made by Mr. Ross in connection with the Heusler alloys. As far as my own work goes, and as far as my ideas go, I agree with his view that there is no evidence in favour of the existence of a ternary compound in the copper-aluminium-manganese system. My observations are confined to a range of 11 per cent. of aluminium and 10 per cent. manganese. In that range there is no evidence of the existence of a ternary compound. I will sketch briefly what we have done.

The range of composition of any system of ternary alloys may be represented by an equilateral triangle, and the parallelogram Cu–Al–Mn represents a corner cut out of such a triangle, covering the range of alloys just mentioned. On this parallelogram the observed alloys are indicated by dots and crosses, dots being used in those cases where the alloy shows no heat-evolution below the freezing-point, while crosses indicate those alloys which exhibit one or more lower heat-evolutions. The dotted line AB marks the course of a valley or ternary minimum in the liquidus surface * of the alloys, and it will be seen that no alloy to the left of this line exhibits more than one lower heat-evolution. Now the alloys lying in the right-hand upper corner of the parallelogram are distinctly magnetic, and Mr. A. Campbell kindly examined the whole series by the most sensitive method available for such rough ingots. It was found that there was a steady decrease of magnetic qualities as the composition of the alloys departed from that indicated by the right-hand top corner of the diagram, and the line MM indicates a limit beyond which no trace of magnetic qualities could be detected. Now it is an important fact that the line MM crosses the line AB at a large angle. If the



magnetic properties were due to the presence of a ternary compound in the magnetic alloys and its absence from the non-magnetic ones, we might well expect the limit of magnetic alloys to coincide with, or to be affected by, that deep ternary valley AB. Further, if it should be a case of a ternary compound formed either by fusion or by reactions in the solid alloys, we should expect to find that some of the heat-evolutions found in these alloys would be co-extensive with the magnetic qualities—but a glance at the diagram, where these heat-evolutions are indicated, at once shows that there is no visible connection between them—these heat-evolutions are obviously related to the line AB and not to the line MM. These facts constitute strong evidence in favour of the view that there is no definite ternary compound whose range of existence determines the range of magnetic qualities. Quite apart from copper, the alloys of aluminium and manganese are strongly

* A model of the liquidus surface, and the diagram here reproduced by kind permission of the Institution of Mechanical Engineers, will be found in the Ninth Report to the Alloys Research Committee, "On the Properties of some Alloys of Copper, Aluminium, and Manganese," by W. Rosenhain and F. C. A. H. Lantsberry, *Proc. Inst. Mech. Engineers*, 1910.

magnetic, particularly near the manganese end of the series, where a definite magnetic compound of the two metals appears to exist. My view is that the Heusler alloys probably owe their magnetic properties to the presence in them, in solid solution, of this aluminium-manganese compound. Much more convincing evidence would be required to justify the supposition that a ternary compound enters into the matter.

Dr. Cecil H. Desch (Glasgow) wrote : The most urgent problem in connection with the Heusler alloys now appears to be that of the relation between their chemical constitution and magnetic properties. The hypothesis originally put forward by Heusler and Richarz, that the maximum of magnetic properties occurs in a series of isomorphous crystals, the end members of which are Mn_3Al and Cu_3Al, is now firmly established, but much yet remains to be done. Recent work in metallography has shown that an intermetallic compound which forms solid solutions with its components may have a temperature range of existence limited both above and below, so that the maximum formation of the compound is only obtained by annealing within that range. Further, much recent work has shown that a metallographic system is not necessarily fully stable when equilibrium has been reached in the sense of the phase rule, that is, when the phases present are entirely those stable at the temperature in question. The phases may first appear in a state of ultramicroscopic subdivision, and annealing leads to segregation to form coarser particles. Physical stability is only reached when this second process is complete. Hence the "ageing" of the Heusler alloys may be a complex effect, caused by (1) the formation of inter-metallic compounds ; (2) the equalisation of composition by diffusion ; (3) the union of ultramicroscopic particles of various phases to form physically more stable aggregates. All of these processes may be concerned in modifying the magnetic properties.

A thorough thermal and microscopical investigation of the alloys is required, and this can only be carried out in a laboratory completely equipped for the purpose. The cooling curves taken by Rosenhain and Lantsberry show how extraordinarily complicated are the thermal changes which occur in solid alloys of copper, manganese, and aluminium. As regards the microscopic structure, the few photographs hitherto published do not give much information, and a very careful study, using high magnifications, is required. In this connection stress may be laid on the necessity of using alloys prepared from pure metals, as commercial manganese contains a considerable quantity of impurities capable of affecting the structure, and it is highly probable that certain micrographic constituents, described as having been observed in magnetic alloys, are really due to impurities, since they are not observed when pure materials are used. The most strongly magnetic alloys of this class appear to be, at least under certain conditions of heat treatment, homogeneous solid solutions, and high magnifications may be required to observe any resolution into new constituents which takes place under different thermal conditions.

Professor E. Wedekind (*communicated after the meeting*) : In the Paper which Dr. Heusler read before the Faraday Society he has made several attacks of a personal character against me which I must refute.

He declares (p. 182) that in my *Magnetochemie* (Berlin, 1911) I have described his observations as accidental and have ascribed to myself alone the merit of discovery of the manganese alloys and compounds. Concerning the accidental character of the first discovery of Heusler there can be no doubt, as is shown by his own words, quoted on p. 44 of my brochure. Hence, it is useless to waste words on this unnecessary

reclamation. The further statement is a direct misrepresentation of the facts of the case, for in the section on the manganese alloys (p. 44 *et seq.*) my name is not even mentioned ; on the contrary, I expressly refer to the description of the first discovery of Heusler (p. 45), saying that he had obtained magnetic alloys with other trivalent metals, As, Sb, Bi, as well as B, and I have never omitted to make full acknowledgment of Heusler's work, wherever occasion required.

As far as Dr. Heusler's observations on manganese-boron are concerned, in order to avoid misunderstanding, it may be here expressly stated that, in 1905, with a written explicit understanding with him, I examined my manganese boride and some other allied compounds with regard to their magnetic properties. One cannot subsequently contradict such an understanding just because it has become inconvenient for some reason.

Further, Heusler is not correct in his statement that he had at that time pointed out that magnetism is a molecular property of *definite* compounds. It was not recognised until much later that magnetisability depends not only on the nature of the components, but also on their stoichiometric composition ; for example, that MnB is ferromagnetic, but MnB_2 is not. If Heusler at this time characterises his manganese-boron melts as mixtures of the borides MnB and MnB_2, then it must be inferred that he has never published particulars of the results of the analyses of the mixtures.* Heusler has therefore no reason for regarding my preparations, the analyses of which accorded with the formulæ MnB and MnB_2, as impure.†

It was just the same with the first qualitative accounts of Heusler with regard to the complexes of manganese with phosphorus, arsenic, antimony, and bismuth ; he did not produce a single definite or analysed compound. Various disagreements with later observations have been explained by investigations in which Dr. Heusler had taken no part, that definite manganese compounds with trivalent elements possess various magnetisability always according to their stoichiometric composition (*e.g.*, MnSb, Mn_2Sb, Mn_3Sb_2). The compound Mn_2As prepared by me, for the existence of which Hilpert and Dieckmann by thermometric methods could find no sufficient evidence, a fact to which Heusler has called attention, was some time ago confirmed by K. Friedrich and P. Schoen (*Metallurgie*, 7 [1912], 739) by a metallographic investigation ; but on this Dr. Heusler is silent. Really Dr. Heusler's communication brings to light no new experimental facts, so that I need not go beyond this defence of the more or less personal remarks.

Dr. E. Take (*communicated*) : Mr. Ross quotes the hypothesis of Heusler, that the compound $Al_x(Mn,Cu)_{3x}$ is the carrier of the pronounced ferromagnetic properties in the Al–Mn bronzes. There is, however, an error as regards the date of the first publication of this hypothesis. A preliminary note on this hypothesis was communicated already on June 6, 1906, to the meeting of the *Marburger Gesellschaft zur Beforderung der gesamten Naturwissenschaften* (*Sitz. Ber.*, 1908, p. 203). The detailed exposition of the hypothesis was afterwards given in the inaugural dissertation of W. Preusser, Marburg, 1908 (presented to the Philosophical Faculty on August 15, 1908), and further by Heusler himself in the *Zeitschrift für anorganische Chemie*, vol. 61, 1909. This latter publication, to which Mr. Ross refers, was

* Heusler showed at the time that there was in his manganese-aluminium-bronze a maximum magnetisability when for one atom of manganese there is one atom of aluminium. However, a compound MnAl does not exist. Much later, therefore, a hypothetical compound $Al_x(Cu_1Mn_3)$ was affirmed.

† Likewise at the time I called special attention unreservedly to the work of Binet du Jassoneix on the separation and purification of the borides (see *Berichte d. deutsch. chem. ges.*, 40, 1907, 1261, 3853).

received by the editors of the journal on October 3, 1908 (compare *Ibid.*, vol. 61, p. 279). It will, moreover, be seen from the paper by Heusler (pp. 275–276) that Heusler had arrived at his hypothesis already in 1907, since the experiments of Preusser were undertaken for the purpose of confirming this hypothesis. There can hence not be any doubt as to the priority of Heusler.

As regards the suggested differences between the theories of Mr. Ross and of Heusler, whether there be solid solutions of the components Cu_3Al and Mn_3Al or the chemical compound $Al_x(Mn,Cu)_{3x}$, Dr. Heusler will deal with this question in another place.

Dr. A. D. Ross (*communicated after the meeting*): I should like to make a brief reference to one or two points mentioned by Heusler and Take in their joint paper on "The Nature of the Heusler Alloys," as I think that some of their statements—particularly in reference to my own work—are rather misleading.

On p. 176, I am referred to as having in papers published in 1910 and 1911 "advocated the same hypothesis which Heusler had, three years previously, submitted to the public already on a well-established basis." The hypothesis referred to is of course that of the existence of a series of ternary chemical compounds of copper, manganese, and aluminium, which Heusler and his colleagues regard as the carrier of the ferromagnetism in these bronzes. I wish to take this opportunity of stating emphatically that, so far from advocating this hypothesis, I have never postulated the existence of such compounds; on the contrary, I have on many occasions (and indeed in one of the two papers cited by Heusler and Take !) stated that I consider this hypothesis to be altogether untenable. My view has been that the ferromagnetism is associated with the occurrence of solid solutions, and the two binary compounds Cu_3Al and Mn_3Al have been mentioned as the probable constituents of these solutions. The first public announcement of my hypothesis was made so long ago as March, 1907, before the Physical Society of Glasgow University, and I advanced additional arguments in its favour at a meeting held twelve months later. In two papers* published early in 1909, Cu_3Al was referred to as one of the constituents of this phase, and in a general paper † published in the following year, the part played by Mn_3Al was discussed. These facts are briefly noted in the paper submitted at this meeting. In addition, I have summarised the arguments which have all along kept me from accepting Heusler's views, and I have given a few facts obtained from thermal and metallographic investigations which I consider are conclusive on this point of our difference. Moreover, Heusler's hypothesis only assumed its present form—that of the existence of ternary compounds of general formula $Al_x(Cu,Mn)_{3x}$—in 1909; at any rate I have no knowledge of its announcement prior to the two papers ‡ referred to by Take as those in which Heusler published his views.

The other point to which I shall refer is that of the influence of the rate of cooling of the alloys on their resultant magnetic properties. Take appears to be under a misapprehension that the quenching and other thermal tests made on these alloys at Glasgow University have been carried out merely in confirmation of his own results.§ On the contrary, the investigation of the effect of thermal treatment on the Heusler alloys was taken up at Glasgow by Professor A. Gray and his assistants in 1904, and certain of the results

* *Proc. Roy. Soc. Edin.*, xxix., 274, 1909; *Proc. Roy. Phil. Soc. Glasgow*, xl., 94, 1909.

† *Journ. Inst. of Metals*, No. 2, iv., 80, 1910.

‡ *Zeitschr. anorg. Chem.*, lxi., 277, 1909; Wallach-Festschrift, 467, Göttingen, Vandenhoeck and Ruprecht, 1909.

§ See Take's paper, p. 9, footnote.

obtained are given in a paper* communicated to the Royal Society in the following year. My own investigations on this subject were carried out in Professor Gray's laboratories, and the first results were communicated at a meeting of the Royal Philosophical Society of Glasgow held early in 1906. A feature noticed in all these earlier tests was the low coercive force of the quenched metal and the high coercive force of the slowly cooled metal. The paper† which I published in 1907 showed clearly how the effect of quenching the alloys in altering both the permeability and the coercive force depended on the temperature at which the quenching was carried out, and it was also pointed out how the magnetic quality of the quenched metal improved on ageing. The reference given by Take on p. 177 would convey the impression that my results were not announced until 1909—that is, after, instead of, as was the case, before the detailed paper‡ of Heusler and Richarz was published in February, 1909.

The Chairman: We none of us wish to part this evening without offering our extremely hearty thanks to those gentlemen who have come from Berlin, Strassburg, Glasgow, Sheffield, and elsewhere, and given us the admirable papers which we have heard this evening. As I said in my opening remarks, I think these papers are of an exceedingly high character indeed. They are evidence of the Society doing good work, and we have never had more interesting papers than those which have been presented this evening.

The proposition was carried by acclamation, and the meeting closed.

* *Proc. Roy. Soc.*, A, lxxvii., 256.
† *Proc. Roy. Soc. Edin.*, xxvii., 88, 1907.
‡ *Zeitschr. anorg. Chem.*, lxi., 265, 1909.

ELECTROCAPILLARY PULSATION OF A MERCURY MENISCUS.

By ALEXANDER P. ROSHDESTWENSKY
AND
WILLIAM C. McC. LEWIS.

[From the Chemical Laboratory of University College, London.]

(*A Paper read before the Faraday Society, Tuesday, July 2, 1912,* Professor Alfred W. Porter, F.R.S., *in the Chair.*)

The periodic pulsations of a mercury meniscus confined in a narrow capillary tube, which dips into an aqueous solution of a mercury salt, were observed accidentally during the progress of some measurements carried out with a view of obtaining a solution for the capillary electrometer which might exhibit greater sensitivity to small changes in e.m.f. than the sulphuric acid solution ordinarily employed. With this object aqueous solutions of mercuric cyanide either alone or in presence of potassium cyanide were prepared, as it was hoped that by this means the concentration of mercury ion could be kept under a more strict control than is possible with sulphuric acid solutions. As a matter of fact, so far as our experiments have yet gone, the ordinary sulphuric acid solution is much more sensitive, and therefore more suitable for the electrometer, than any other solution investigated. It was considered, however, that the pulsation effect (which was not observed with sulphuric acid solutions of the concentration examined, but came prominently into view with a certain concentration range of mercuric cyanide) merited some further examination for its own sake.

The movements of mercury surfaces in contact with various substances have been observed previously in a number of instances. Thus Wiedemann* quotes in connection with the subject of polarisation some instances of the pulsation of large mercury surfaces in contact with various aqueous solutions. The general view which seems to be held with regard to such effects is that they are due to the formation of films of insoluble mercury salts whose presence alters the surface tension—or rather the interfacial tension—of the mercury. When these films grow to some thickness they may be mechanically broken and the process of reformation begins. As a rule the systems examined are of a very heterogeneous nature, relatively large masses of mercury having crystals of various substances lying on the surface under the water layer. Movements of the crystals similar to those of camphor on water have been described. The movements of the mercury surface itself have been most frequently observed when in contact with acid solutions containing crystals of very chemically active substances, such as potassium bichromate or permanganate, the crystals being in the act of dissolving. The vibration of the mercury and streaming of its surface in different directions have been observed without the application of any electromotive force. In cases in

* *Elektricität*, vol. ii., p. 735 (1894).

which an e.m.f. was applied the mercury was generally made the anode. The measurements and results are ill-defined and fragmentary, and such effects as those referred to may not even be connected in any way with the effects to be described later. Even the observations of K. Schaum* on the motion of dissolving crystals lying on a mercury surface do not in any way clear up the mechanism of the contact surface effects. The only discussion of these phenomena in which it is explicitly suggested that electrocapillary forces are the cause is that of A. Thiele.† More recently an important study of a pulsating mercury surface in contact with an aqueous solution has been made by von Antropoff‡ in dealing with the phenomenon of "pulsating catalysis of

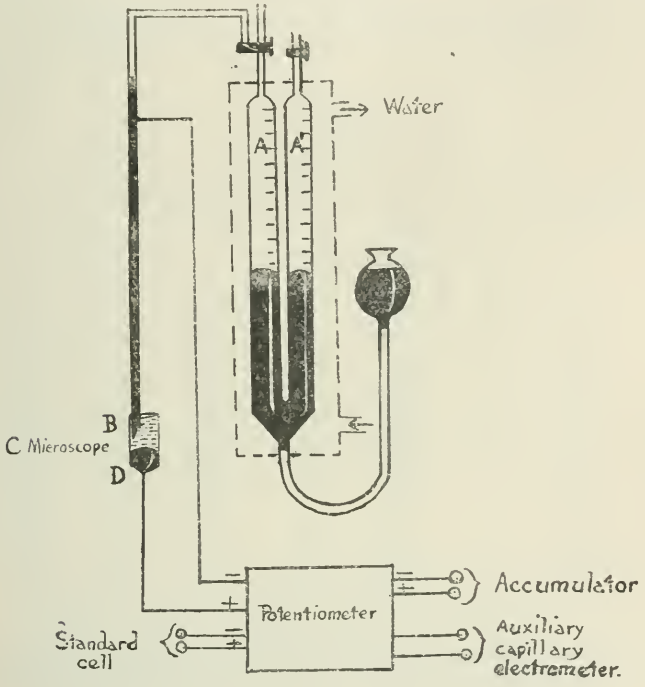


FIG. 1.

hydrogen peroxide decomposition" by means of the mercury surface. In this case the pulsation has been traced to the formation and subsequent mechanical disintegration of a film of a mercury peroxide, this new compound being actually isolated by von Antropoff. Since the pulsation in this case is due to the formation of a compound resulting from the presence of hydrogen peroxide in the solution, the same substance cannot of course be regarded as the cause of the pulsation of a mercury meniscus inserted in solutions of mercuric cyanide, and we have been unable to obtain any optical evidence of formation of films or layers of insoluble substances even after the meniscus has been long in contact with the solution.

So far as the authors have been able to find no previous observations have been made of the pulsation of a mercury column in a fine capillary tube

* *Physikal. Zeitschr.*, 1899, **1**, 5.
† *Zeitschr. für Elektrochem.*, 1906, **12**, 257.
‡ *Zeitschr. physik. Chem.*, 1908, **62**, 513.

under a certain range of applied e.m.f. and with solutions of certain composition.

The Apparatus Employed.

The apparatus shown in Fig. 1 fairly closely resembles that of Lippmann,* with the exception that the alterations in pressure necessary to bring the meniscus to the zero position after altering the applied e.m.f. were brought about by raising or lowering the mercury in a graduated burette A, connection being established between A and the vertical mercury column which was supported by and ended in the capillary B. The burette A^1 was united to A at the bottom and opened to the atmosphere at the top, and the difference in height between A and A^1, which could be read by a telescope, gave the increase or decrease in pressure required to bring the meniscus in B to the zero point. The burettes A and A^1 were enclosed in a water-jacket to keep

Table I.

Sulphuric Acid.

Applied e.m f.	Δp.	Applied e.m.f.	Δp.
	mm. Hg.		mm. Hg.
0	0	0·13	56·7
0·01	11·3	0·20	79·0
0·02	12·8	0·30	112·7
0·03	15·3	0·40	139·0
0·04	19·0	0·50	161·8
0·05	24·5	0·60	177·0
0·06	29·7	0·70	189·4
0·07	33·5	0·80	195·5
0·08	36·5	0·90	199·6
0·09	40·7	1·0	194·7
0·1	44·5	1·1	184·6
0·11	48·6	1·2	179·0
0·12	53·2	1·3	158·0

the temperature of the mercury constant. The solution to be examined was placed in a test-tube having a quantity of mercury D at the bottom, to which electrical connection was made from the potentiometer terminal. By means of a platinum wire sealed into the vertical capillary mercury column electrical connection was made to the other potentiometer terminal as shown in the figure. In the measurements to be described the mercury of the meniscus (B) was the negative pole, D being the positive pole. The potentiometer (a good type made by the Land- und Seekabelwerke) and its connections, accumulator, Weston standard cell, and auxiliary capillary electrometer (for balancing the standard cell and accumulator so that known voltages could be tapped off at the B and C terminals), call for no remark. The highest e.m.f. which could be applied between B and D was 1·5 volt.

Measurements with Sulphuric Acid Solution.

The solution was that employed by Lippmann, consisting of 1 volume concentrated acid and 9 volumes of water. The table above (Table I.) contains the results obtained, the direction of the current being from D to B

* *Annales de Chim. et de Phys.*, 1875, 5, 531.

inside the solution. The symbol Δp denotes the increase in pressure required to bring the meniscus at B back to the zero point. The zero point is the position of the meniscus when no e.m.f. is applied and the columns A and A^1 are at the same level. Δp is simply the difference of the readings in A^1 and A. The capillary in B was very fine, namely of the order 0·02 mm. This supported a column of mercury 580 mm. in height when dipping into the sulphuric acid solution.

The maximum of the interfacial tension occurs when the applied e.m.f. is 0·9 volt. The curve obtained on plotting these data shows the usual peculiarity

TABLE II.

$\frac{N}{10}Hg(CN)_2$. *Height of Column above B = 550 mm.*

Series of Observations.	(*a*.)	(*b*.)	(*c*.)	(*d*.)	(*e*.)	(*f*.)
Applied e.m.f	Δp.	Δp.	Δp.	Δp.	Δp.	Δp.
0	0 mm.	0	0	0	—	—
0·05	35	34	—	—	—	—
0·3	—	—	— 2	— 2	—	—
0·4	48	—	1	1	1	1
0·5	—	—	5	6	5	5
0·6	59	59	9	9	9	—
0·7	—	—	14	14	13	—
0·8	37	38	12	12	12	—
0·9	25	26	9	—	11	—
1·0	10	—	9	—	10	9
1·1	—	—	25	—	25	26
1·2	—	—	27	—	26	29
1·3	30	30	30	—	29	30
1·4	—	—	—	—	31	31
1·5	—	—	—	—	32	—

Region of pulsation. (1·0 – 1·5)

Region of pulsation. (1·1 – 1·4)

REMARKS.

Series (*a*) and (*b*) were made consecutively on the same day with the same solution. The time taken for any one series is about two hours. (*a*) and (*b*) agree well with one another.

Series (*c*) to (*f*) were made consecutively on the same day. They agree with one another but differ widely from (*a*) and (*b*).

The capillary maximum occurs at the same point for all series (*a*) to (*f*), viz., when applied e.m.f. is 0·7 volt.

of having the ascending portion slightly steeper than the descending. From the agreement of Lippmann's results with our own, it was concluded that this form of the apparatus worked satisfactorily; and it was inferred therefore that the peculiarities observed in the mercuric cyanide solutions possessed a real significance.

MEASUREMENTS WITH MERCURIC CYANIDE SOLUTIONS.

The following solutions were examined :—

Saturated $Hg(CN)_2$ (at 15° C.)
$\frac{N}{10}Hg(CN)_2$
$\frac{N}{100}Hg(CN)_2$
$\frac{N}{1000}Hg(CN)_2$

$\frac{N}{10}Hg(CN)_2 + \frac{N}{10}KCN$
$\frac{N}{100}Hg(CN)_2 + \frac{N}{10}KCN$
$\frac{N}{1000}Hg(CN)_2 + \frac{N}{10}KCN$

In these solutions the first point noticed was the irregularities in the Δp values for any given applied e.m.f. The determinations made on the same day agreed well with one another, but after standing in contact with the mercury for twenty-four hours or more, the values obtained differed largely from those given by the fresh solution. This is evidently an ageing effect, and suggests a gradual approach to an equilibrium stage. The important point is, however, that the position of the maximum surface tension varied only very slightly with the age of the solution, so that the e.m.f. which caused the maximum in the case of a fresh solution likewise caused a maximum in the old. Further, the value of the applied e.m.f. at which the *pulsation* just

TABLE III.

$\frac{N}{10}Hg(CN)_2$. *Height of Column above B = 430 mm.*

Series of Observations.	(*g*.)	(*h*.)	(*i*.)	(*k*.)	(*l*.)
Applied e.m.f.	Δp.	Δp.	Δp.	Δp.	Δp.
0·1	88 mm.	89	41	67	—
0·2	101	102	50	82	73
0·3	101	105	53	81	73
0·4	101	105	54	82	75
0·5	103	109	52	80	78
0·6	109	111	51	85	79
0·7	112	114	—	—	85
0·8	118	121	—	90	92
0·9	128	129	74	98	97
1·0	122	122	65	92	85
1·1	109	110	58	98	99
1·2	124	123	65	102	101
1·3	124	123	72	—	101
1·4	124	123	72	—	101
1·5	124	123	72	—	101

Region of pulsation. (1·0 – 1·2)

Region of pulsation. (1·3 – 1·5)

REMARKS.

Series (*g*) and (*h*) were made consecutively on the same day.

Series (*i*) (*k*) (*l*) were made with a solution which was freshly prepared for series (*i*) and was allowed to stand over mercury twenty-four hours before (*k*) and (*l*) were consecutively carried out.

Series (*g*) and (*h*) agree with one another.

Series (*i*) (*k*) (*l*) are discordant.

It will be observed that the capillary maximum occurs at the same point in all series, viz., at e.m.f. 0·9 volt. The maximum appears to occur at a different point from that of Table II. It depends, therefore, on the height of the column above *B*.

began to appear was practically the same in fresh and old solutions alike. In Table II. are given by way of example the data for a single case. A reproduction of similar variations obtained in the other cases would be of little value. It is possible, however, to draw curves which are characteristic of the type of electrocapillary behaviour in the different cases, and these are given later.

Data obtained with $\frac{N}{1}Hg(CN)_2$.—With the capillary chosen for the first series of measurements, the height of the vertical mercury column above was 550 mm.; in the second series a new capillary was employed, the height being 430 mm. As in the sulphuric acid case, the position of the meniscus—the zero

position—was perfectly well defined, there being no oscillation with applied e.m.f. = 0. Δp, as before, denotes the difference in height between the columns A^1 and A required to bring the meniscus to its zero point. As already mentioned, when the pulsation region was reached, the value of Δp represents the increase in pressure required to bring the mercury to such a position that its upper limit of oscillation just coincided with the zero point (although this may not be perhaps comparable with the readings when no pulsation occurs).

Fig. 2 represents the general shape of the curve which would reproduce the type of electrocapillary behaviour of the above case. It will be observed

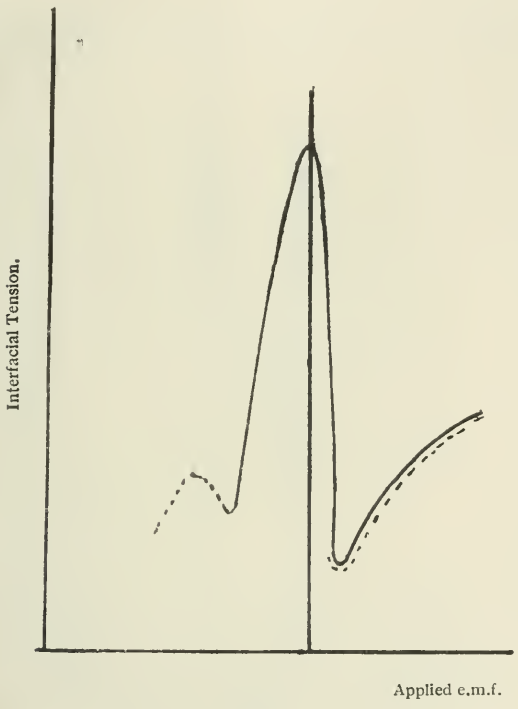


FIG. 2.

$\frac{N}{10}$ $Hg(CN)_2$. Maximum at 0·7–0·9 volt.

that after passing through the maximum surface tension the tension falls until pulsation commences (at 1·1 volt approximately) and thereafter appears to rise. This behaviour was, however, not observed in saturated $Hg(CN)_2$ solutions (Fig. 5), although pulsation occurred. In the diagrams, the region of pulsation is denoted by full and dotted lines side by side and the solutions to which the curve refers are also given.

DESCRIPTION OF THE PULSATION.

The following are the chief characteristics observed, a solution of $\frac{N}{10}$ $Hg(CN)_2$ being chosen as a typical instance. The capillary supported a mercury column 550 mm. in height, the diameter at the zero position of the meniscus being 0·026 mm. No pulsation was observed until the applied e.m.f. was raised to 1 volt, the capillary mercury being the cathode. On closing the

circuit the mercury meniscus was seen to rise* slowly for about 6 minutes, and then commenced to pulsate when it had reached 2·5 eyepiece divisions above zero (one eyepiece division = 0·02 mm.). The columns A and A^1 were kept at the same level. The amplitude of each pulsation was barely 1 division. By raising the mercury in the burette until A^1 differed from A by 9 mm. the pulsation was made to take place in such a way that the zero point coincided with the highest point reached in any pulsation. The periodic time of a complete oscillation was 12 seconds. These pulsations were continuously repeated with great regularity as long as observation lasted (one to two hours).

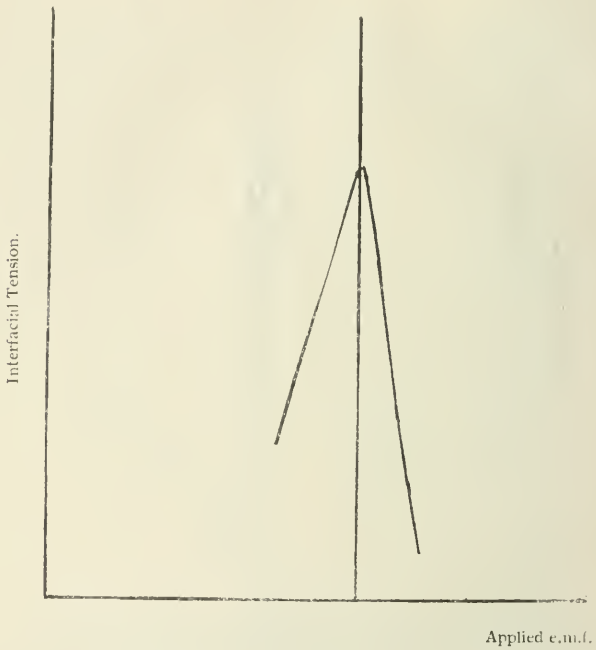


FIG. 3.

$\frac{N}{100}$ $Hg(CN)_2$. Maximum at 0·7 – 0·9 volt.

$\frac{N}{10}$ $Hg(CN)_2$ + $\frac{N}{10}$ KCN. Maximum at 0·4 volt.

$\frac{N}{100}$ $Hg(CN)_2$ + $\frac{N}{10}$ KCN. „ „ 0·1 „

$\frac{N}{1000}$ $Hg(CN)_2$ + $\frac{N}{10}$ KCN „ „ 0·2 „

When 1·1 volt was inserted and A and A^1 kept at the same level, pulsation set in as before after the steady rise lasting 6 or 7 minutes. The amplitude of vibration was 2 eyepiece divisions, and the periodic time 9 seconds. When A^1 is made 25 mm. higher than A, the highest point reached in an oscillation corresponds to the zero position of the meniscus (zero being the position occupied when no e.m.f. is applied and $A^1 - A = 0$). Under these conditions the amplitude is 3·25 divisions, the periodic time being 6 to 7 seconds.

* In the telescope the direction of motion was, of course, reversed. The words "rise" or "fall," as used in the text, refer to the actual motion of the mercury, not to the movements as seen in the eyepiece.

When the applied e.m.f. is 1·2 volts and A^1 and A are level, after the usual slow upward movement, the pulsation begins from the third eyepiece division above the zero to the second below zero, in all five divisions, the periodic time being 13–14 seconds. When $(A^1 - A)$ is made 15 mm. difference in height, the pulsation occurs between 1·5 divisions above zero and 4·5 divisions below zero, in all 6 divisions, the time taken being 12 seconds. Finally, when the pressure is adjusted ($A^1 - A = 26$ mm.) so that the pulsation takes place between zero and 6 divisions below, the time required is again 12 seconds.

When 1·3 volts is employed practically the same effects are observed as in the above. It will be noticed that as the applied e.m.f. increases the amplitude of the pulsation increases, but there does not appear to be any corresponding change in the periodic time.

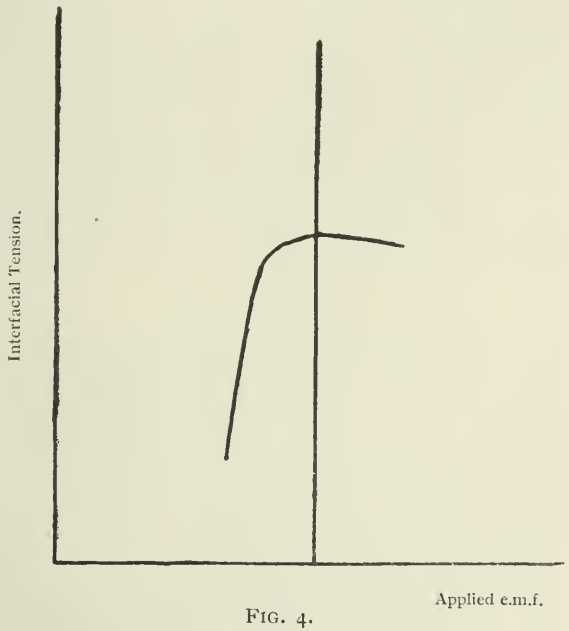


FIG. 4.

$\frac{N}{1000}$ $Hg(CN)_2$. Maximum 0·7 – 1·0 volt.

With 1·5 volts inserted the pulsation behaviour becomes more marked still, and it is possible to divide the whole process into an initial stage and three stages of pulsation. The initial stage is, as before, a slow rise of the meniscus, corresponding therefore to a steady increase in the interfacial tension. This takes about 6 minutes to complete itself, and when A^1 and A are at the same level it was observed that the maximum point reached was 4 divisions above zero. The meniscus then began to fall, at first slowly over 2 divisions—this, the first stage of the pulsation proper, requiring 35 seconds. This was succeeded by a more rapid fall to the tenth division below zero—the time taken for this, the second stage, being only 3 seconds. The mercury then rose quickly to the fourth division above zero, thereby completing the third stage of the pulsation, after which the pulsation proper (stage one) recommenced. The amplitude in this case is large, namely

14 divisions, the periodic time being a little over 38 seconds. When the columns A^1 and A were given various values the phenomena appeared to be the same, no regular effect being ascribable to such pressure changes, except that the pulsation did not occur at quite the same position in the capillary. When A^1 is 32 mm. higher than A, the maximum point reached in a pulsation coincided with the zero point, the amplitude of oscillation being 12 eyepiece divisions. The time taken for the first pulsation stage was 25 seconds, the rapid second and third stages requiring about 5 seconds, making the total period about 30 seconds. No stress can be laid, however, on the difference between this value and the preceding.

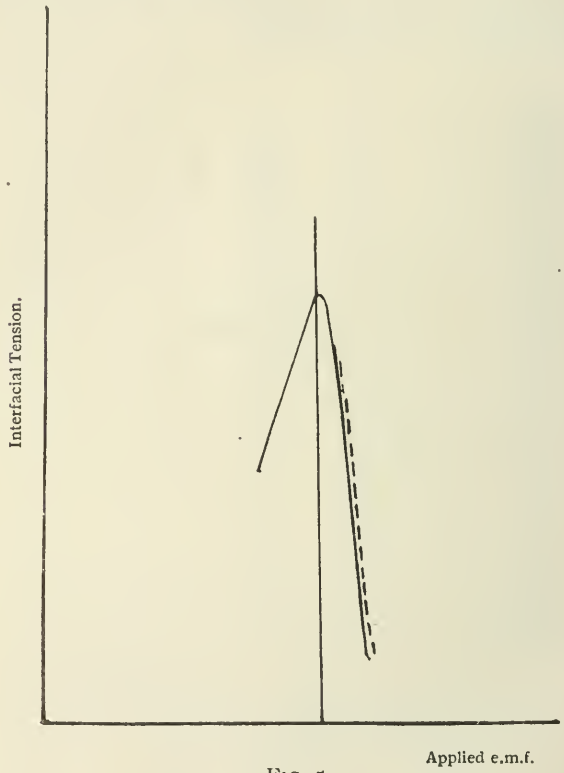


FIG. 5.

Saturated $Hg(CN)_2$. Maximum at 0·8–1·0 volt.

It may be mentioned that the effects above described were reproduced many times with different solutions and different capillary tubes. Further, the ageing of the solutions—by allowing them to remain in contact with mercury for twenty-four hours or more—produced very little effect on this behaviour.

CONDITIONS LIMITING THE EXISTENCE OF PULSATIONS.

The occurrence of pulsation is determined by three factors—(1) the value of the applied e.m.f., (2) the diameter of the capillary, and (3) the nature of the solution.

In all cases examined so far the oscillation did not make its appearance

until at least an e.m.f. of 1 volt had been applied, the capillary mercury being the cathode. The pulsation increased in amplitude as the e.m.f. increased.

The size of the capillary is also of great importance. It was found, for example, that with a capillary so fine that it was able to support a column of mercury 700 mm. in height, *no pulsation occurred under any e.m.f. applied in any of the solutions examined.* The diameter in this case would be somewhat less than 0·02 mm., though we do not know it more accurately. Pulsation—say with a decinormal solution of mercuric cyanide—was observed with a capillary which was able to support a column 570 mm., and likewise with a wider capillary capable of supporting a column of 430 mm. height. With this latter capillary also pulsation was observed with a certain solution—saturated $Hg(CN)_2$—while using the same solution no pulsation could be observed with the narrower capillary capable of supporting 570 mm. mercury. We have not yet investigated whether there is any upper limit (as regards width) to the diameter of a capillary capable of exhibiting pulsation effect for a given solution. There is evidently a lower limit, as already pointed out.

With regard to the nature of the solution, it has already been pointed out that while $\frac{N}{10}Hg(CN)_2$ and saturated $Hg(CN)_2$ showed pulsation with a suitable capillary, no pulsation has yet been observed with the more dilute solutions $\frac{N}{100}$ and $\frac{N}{1000}$ $Hg(CN)_2$. Similarly no pulsation was observed with the solutions containing potassium cyanide, viz.: $\frac{N}{10}Hg(CN)_2 + KCN\frac{N}{10}$; $\frac{N}{100}Hg(CN)_2 + \frac{N}{10}KCN$; $\frac{N}{1000}Hg(CN) + \frac{N}{10}KCN$.

These limitations are interesting as suggesting that *the mercury ion concentration must not be too low*, but beyond this qualitative conclusion we have not yet gone.

Discussion of Results.

The pulsations described appear to manifest themselves only when the applied e.m.f. is of such magnitude that the natural p.d. of the interface mercury/solution has been annulled (assuming that such takes place in the region of maximum surface tension, which is not by any means an absolutely safe criterion), and the pulsations persist throughout the region in which the mercury is negatively charged with respect to the solution. The "natural" charge on the mercury surface has therefore to be at least removed before visible pulsation sets in. In the experimental arrangement chosen it is evident that a small electrolysis must be continuously going on, $Hg^{\cdot\cdot}$ or $Hg_2^{\cdot\cdot}$, or perhaps some complex cation, being carried towards the capillary mercury surface, since this is the cathode. If we consider the electrical effect produced by the cations approaching the surface it is clear that they would tend to induce a charge of opposite sign, that is, they would cause the mercury to become more negatively charged with respect to the solution. Since, however, the mercury is already either at zero p.d. or negatively charged with respect to the solution (owing to the applied e.m.f.), the induction effects of the approaching ions would tend to increase the charge already on the mercury surface, and this would decrease the surface tension. The initial stage in the pulsation phenomenon is, however, a slow upward movement of the mercury, which means a slow *increase* in the surface (or rather interfacial) tension. The initial step cannot therefore be explained as a simple induction effect due to approaching cations, although the next step (the first stage of the pulsation proper), which consists of a fall in tension, might legitimately be ascribed to induction effect. Let us consider other effects which might enter into this initial rise in tension. The salt investigated happens to have been a mercuric salt, and such in the presence of mercury might be partially reduced to the mercurous state, though this should occur, one would think, as readily

without any e.m.f. being applied; under which condition, however, absolutely no pulsation is observed. (We do not know as yet whether mercuric salts in contact with mercury have a lower interfacial tension than mercurous salts, and whether gradual reduction might be observed in this way.) Against the view that reduction is the cause of any part of the pulsation may also be urged the fact that solutions which had been in contact with the mercury for twenty-four hours behaved in practically the same way as fresh solutions. The extension of the work to mercurous salts must, however, be undertaken before any definite conclusion can be come to regarding this point.

As regards the pulsation itself, its slowness (its period being of the order of half a minute) suggests that diffusion effects are probably coming in, an adsorption layer being gradually built up at the surface, which is mechanically broken and again reformed after the stirring which has taken place in the capillary owing to the sudden movement of the mercury. It should be noted that we are here dealing not with a simple case of capillary adsorption, but with the more complicated electrocapillary adsorption, about which so little is known that it would be futile to consider it further at this stage. The fact that there is pulsation at all, *i.e.*, intermittent changes in the value of the interfacial tension, seems only to be accounted for by the assumption of periodic transfers of electricity across the boundary.

In fact, the observation made that the pulsation could be divided into three parts—first a slow creep of the mercury for 30 seconds, followed by a rapid jump in the same direction and an immediate return to zero—is quite analogous to the case of a leaky condenser which is being gradually charged up until finally the insulation breaks down. The accumulation of cations, whether due to capillary or to electrolytic movement of the ions, would go on, depending on the rate at which the ions approach the surface and forming a double layer, the ions inducing a greater and greater negative charge on the mercury, thereby lowering the tension until the potential across the double layer becomes too great for the medium and deposition of metal occurs. This would momentarily cause a sudden fall in the p.d., whereby the mercury would rapidly return to its original position, with consequent stirring of the solution in the neighbourhood. The conditions would thus be once more those of the first stage.

It is not claimed that the above considerations are anything more than a crude outline, the only value of which may be to suggest further experimental work.

SUMMARY.

Lippmann's electrocapillary measurements with sulphuric acid solution have been repeated and confirmed, using a somewhat modified form of his apparatus. No abnormal results were obtained. With other solutions—mercuric cyanide solutions—it was accidentally observed, however, that the meniscus under given conditions is not at rest but oscillates regularly round a mean position. The occurrence of this pulsation is confined within fairly narrow limits, the determining factors being: (1) size of capillary; (2) magnitude of e.m.f.; (3) concentration of mercury ions.

DISCUSSION.

The Chairman remarked that the only experiments which he called to mind at all bearing on those now made by Dr. Lewis were some by Mr. Rollo Appleyard,* leading up ultimately to the design of a special coherer by Sir O. Lodge.† In Mr. Appleyard's experiments globules of mercury, when

* *Proc. Phys. Society*, 1897. † *Proc. Roy. Soc.*, 1903.

made the negative electrode, sent out tentacles towards the positive globule, the length of the tentacle depending upon the current and the distance between the globules. He did not remember that any very definite theory had been put forward to explain the effects produced, though there was little doubt that the movements were a consequence of variations of surface tension. The peculiarity of Dr. Lewis's experiments was the fluctuating character of the effect produced. Although the explanation of this that he put forward was only a qualitative one, it was extremely plausible, and the Society would look forward to further confirmation of it—of a quantitative kind if possible.

ON THE VARIATION OF THE CONDUCTIVITY OF ALUMINIUM ANODE-FILMS WITH TEMPERATURE.

By G. E. BAIRSTO, M.Sc., B.Eng.

(*A Paper read before the Faraday Society, Tuesday, July 2, 1912,* Professor Alfred W. Porter, F.R.S., *in the Chair.*)

In a previous Paper * it was shown that in the few cases tried, and there mentioned, the variation of the leakage current of Al anode-films with temperature followed an exponential law, *i.e.*—

$$i = A\varepsilon^{a\theta}$$

or—

$$\log i = \log A + a\theta$$

the curves obtained by plotting $\log i$ to θ being straight lines over the whole range of temperature from ordinary temperature to the boiling-point of the electrolyte. It was also shown that a was independent of the formation period.

A more extended investigation having proved that this law is obeyed in a very large number of cases, it would seem to demonstrate the fact that the law has some electro-chemical or perhaps physical significance, and is not merely an empirical relationship. It is therefore thought worth while to give an account of these more complete experiments.

The chief variables that may influence these results are :—

1. The time of formation ;
2. The electrolyte ;
3. The voltage of formation ;
4. The concentration of the electrolyte ,
5. The voltage used during the test ;

and we will now consider them in turn.

1. *The Influence of the Time of Formation.*

Fig. 1 and Table I. give the results obtained for saturated Am_2HPO_4 for three different formation periods, viz., twelve hours, one day, and four days respectively. The curves show a rapid increase of the current with temperature. Fig. 2 gives the same results with $\log i$ plotted to the temperature. It will be seen that they give very good straight lines, and moreover the lines are all parallel with one another, the actual values of a and A being :—

	Am_2HPO_4, 100 Volts.		
	12 Hours	1 Day	4 Days
a	0·0622	0·0612	0·0612
A	33·9	20·9	11·7

* *Trans. Faraday Soc.*, vol. vii., 1911, p. 1.

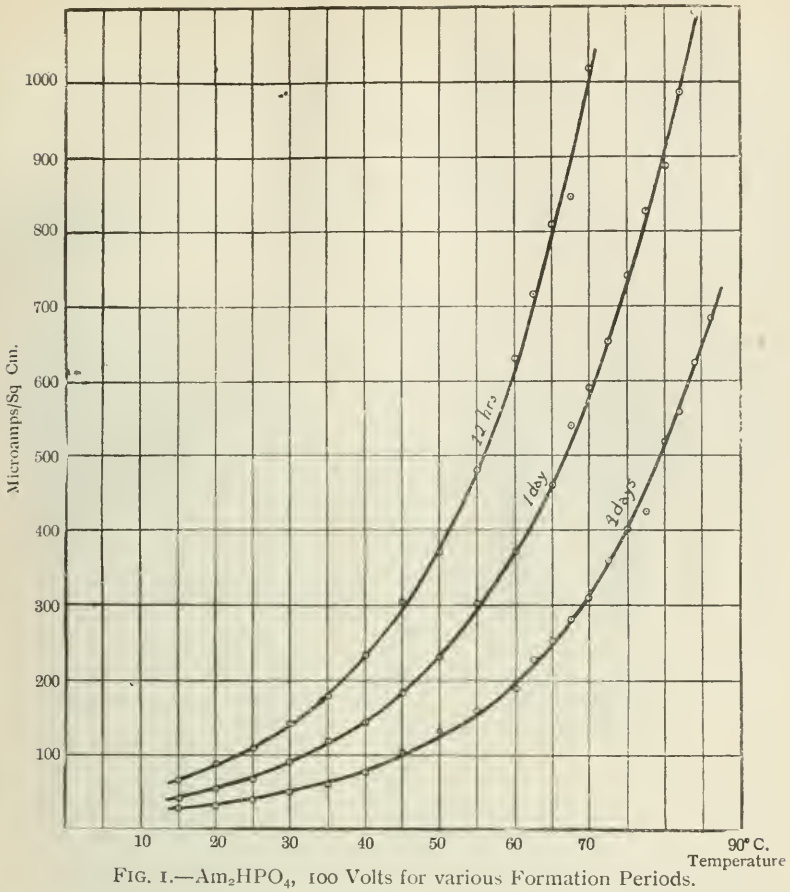


FIG. 1.—Am_2HPO_4, 100 Volts for various Formation Periods.

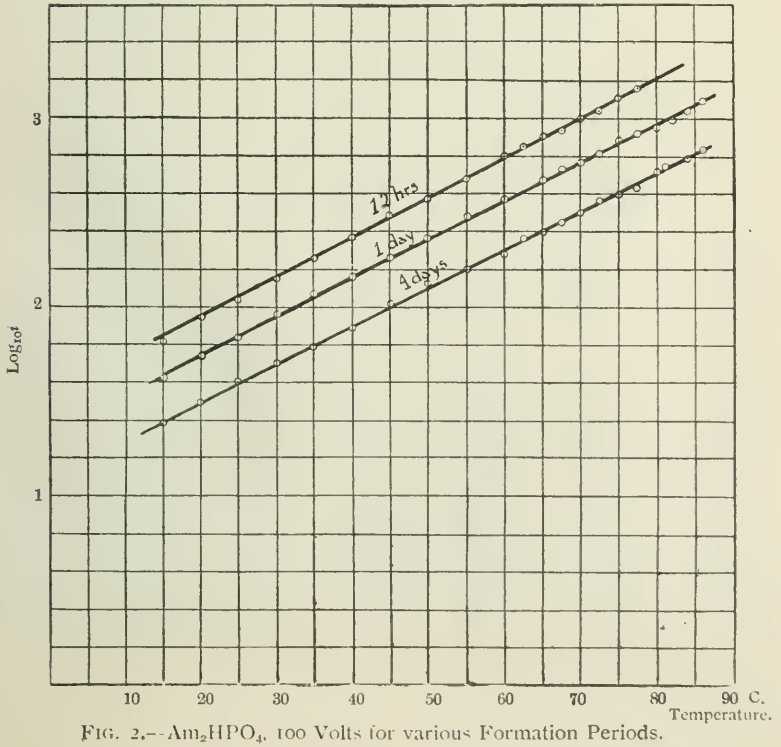


FIG. 2.—Am_2HPO_4, 100 Volts for various Formation Periods.

TABLE I.

Am_2HPO_4. 100 *Volts.*

Temp. ° C.	Half Day.		One Day.		Four Days.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
15	66	1·82	41·8	1·62	23·8	1·38
20	87	1·94	55·4	1·74	31	1·49
25	108	2·03	69	1·84	40	1·60
30	141	2·15	91	1·96	49·5	1·70
35	179	2·25	119	2·07	61	1·79
40	233	2·37	144	2·16	77	1·89
45	303	2·48	183	2·26	104	2·02
50	372	2·57	232	2·36	132	2·12
55	480	2·68	303	2·48	159	2·2
60	630	2·80	372	2·57	189	2·28
62·5	716	2·85	—	—	228	2·36
65	810	2·9	461	2·67	253	2·40
67·5	847	2·93	542	2·73	281	2·45
70	1,020	3·01	592	2·77	310	2·5
72·5	1,190	3·04	653	2·82	360	2·56
75	1,290	3·11	740	2·88	400	2·6
77·5	1,440	3·16	827	2·92	425	2·63
80	—	—	888	2·95	520	2·72
82	—	—	985	2·99	560	2·75
84	—	—	1,095	3·04	625	2·8
86	—	—	1,250	3·09	685	2·84

TABLE II.

$(Am_2O)_{37}(MoO_3)$. 25 *Volts.*

Temp. ° C.	Half Day.		One Day.		Four Days.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
20	20·1	1·30	13·2	1·12	9·0	0·95
25	28·8	1·46	18·6	1·27	13·2	1·12
30	38·5	1·59	26·8	1·43	18·3	1·26
35	52·5	1·72	—	—	26	1·41
40	81·2	1·91	52	1·72	39·4	1·62
45	115	2·06	76	1·88	55	1·74
50	163	2·21	102	2·01	88	1·89
55	238	2·38	144	2·16	105	2·02
60	322	2·51	202	2·31	147	2·17
62·5	384	2·58	—	—	169	2·23
65	442	2·65	285	2·45	195	2·30
67·5	529	2·72	348	2·54	240	2·38
70	655	2·82	417	2·61	292	2·47
72·5	798	2·90	510	2·71	390	2·59
75	962	2·98	615	2·79	472	2·67
77·5	1,130	3·05	745	2·87	605	2·78
80	—	—	850	2·93	—	—

that is to say, while the effect of increasing the time of formation is to decrease the initial value A, in the expression $i = A\epsilon^{a\theta}$, it has no influence on a.

Table II. and Fig. 3 give the results for $(Am_2O)_37(MoO_3)$ for the same three periods of formation, but for a much lower voltage, viz. 25. As before, a is independent of the time of formation, being 0·0910, 0·0895, and 0·0910 respectively.

2. *The Influence of the Electrolyte.*

Fig. 4 shows how the various electrolytes that were tried follow the exponential law. The experimental results are given in different tables, and the curves, with the exception of the $Am_2C_2O_4$, all refer to one particular voltage and period of formation, viz., 100 volts and one day respectively.

The only exception to the exponential law is in the case of $AmHCO_3$, the anomalous behaviour of which electrolyte is considered later on.

The values of a for the five electrolytes are as follows :—

Electrolyte (Saturated)	Value of a in $A\epsilon^{a\theta}$
$Am_2B_4O_7$	0·1090
$AmHCO_3$	0·09255
$(Am_2O)_37(MoO_3)$	0·0890
$Am_2O_2O_4$	0·0865
Am_2HPO_4	0·0612

3. *The Influence of the Voltage of Formation.*

Table IV. and Fig. 5 give the results obtained with Am_2HPO_4 for a formation period of one day, but for different voltages of formation. The lines are practically parallel with one another, the actual values of a being 0·0610, 0·0608, and 0·0612, for 25, 50, and 100 volts respectively, showing that a is independent of the voltage of formation.

Table V. and Fig. 6 give a similar set of results for $(Am_2O)_37(MoO_3)$. Again we have nearly parallel straight lines, the values of a being ·0895, ·0880, and ·0890.

Finally, in Table VI. and Fig. 7 are given the results for $Am_2C_2O_4$, which is an electrolyte with a low critical voltage, and a very considerable leakage current. Since its critical voltage at ordinary temperatures is in the neighbourhood of 100, and an Al anode-film formed in it would therefore fail as the temperature rises, the 100-volt curve it is impossible to give, but even at 50 volts it will be seen that the line is straight, and even in this case the value of a is independent of the voltage of formation.

The exception to the general law mentioned in section 2, *i.e.*, $AmHCO_3$, will now be considered. In Table VII. are given the results for saturated $AmHCO_3$ for the three different voltages, and for a formation period of one day and the log curves are depicted in Fig. 8. It will be noticed that these are straight lines up to a temperature of about 55°, at which point there is an abrupt change, and the curve proceeds along another straight line which is not as steep as in the first stage. The initial lines for the three voltages are, nearly parallel to each other, but not so closely parallel as in the previously mentioned examples—a in fact decreases as the voltage increases (as shown in the following table (p. 240).

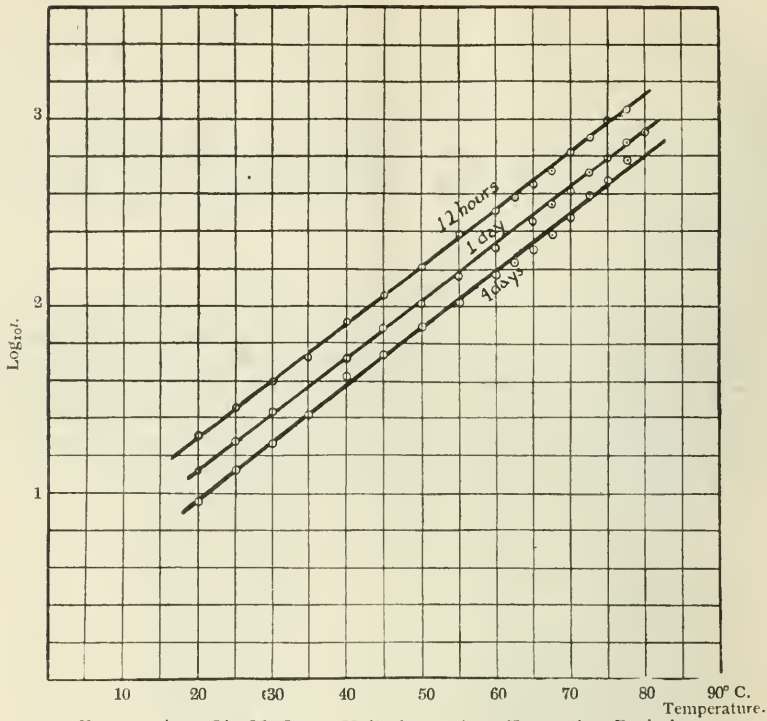


FIG. 3.—$(Am_2O)_3 7MoO_3$, 25 Volts for various Formation Periods.

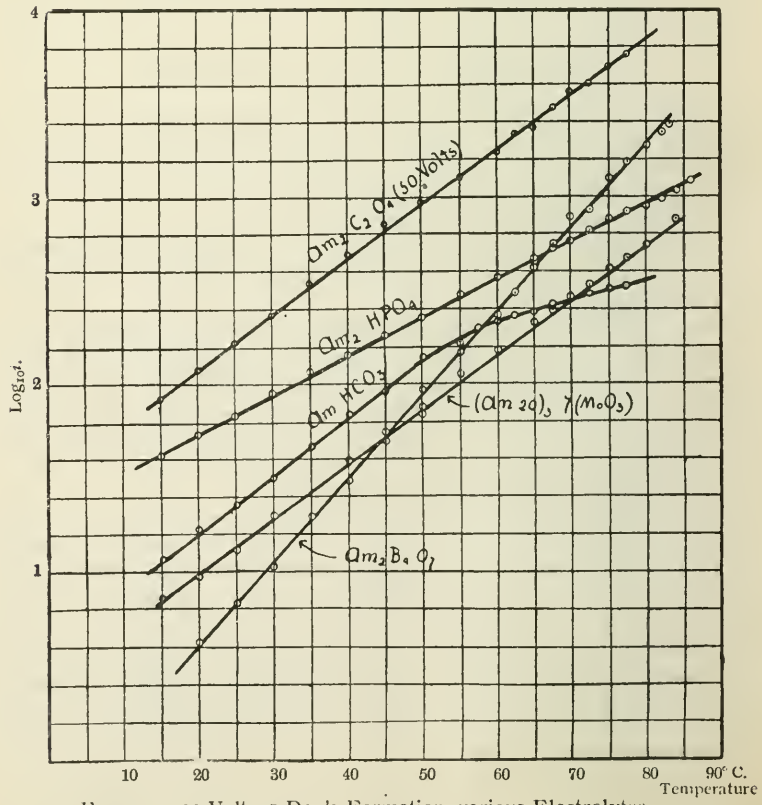


FIG. 4.—100 Volts, 1 Day's Formation, various Electrolytes.

TABLE III.

Formation Period 1 *Day.* 100 *Volts.*

Temp. ° C.	$(Am_2O)_{37}(MoO)_3$.		$Am_2B_4O_7$.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
15	7·1	·85	—	—
20	9·35	·97	4·3	·63
25	13·2	1·12	6·65	·82
30	19·8	1·3	10·8	1·03
35	—	—	21	1·30
40	39·2	1·6	30·7	1·49
45	56	1·75	50·2	1·70
50	78·2	1·88	94	1·97
55	111·5	2·05	147	2·17
60	151	2·18	233	2·37
62·5	—	—	306	2·49
65	213	2·33	416	2·62
67·5	247	2·39	562	2·75
70	290	2·46	780	2·89
72·5	349	2·53	845	2·93
75	408	2·61	1,260	3·10
77·5	465	2·67	1,560	3·19
80	543	2·74	1,910	3·28
82	—	—	2,250	3·35
83	—	—	2,470	3·39
84	765	2·88	—	—

TABLE IV.

Am_2HPO_4. *Formation Period* 1 *Day.*

Temp. ° C.	25 Volts.		50 Volts.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
15	61·3	1·79	48	1·68
20	77·0	1·89	63·6	1·80
25	88·1	1·99	79·6	1·98
30	123	2·09	104	2·02
35	154	2·19	136	2·13
40	189	2·28	168	2·23
45	240	2·40	190	2·29
50	343	2·53	278	2·44
55	395	2·60	—	—
60	—	—	412	2·61
62·5	440	2·76	—	—
65	—	—	526	2·72
67·5	654	2·82	—	—
70	762	2·88	696	2·84
72·5	885	2·95	742	2·87
75	1,020	3·01	872	2·94
77·5	1,140	3·06	946	2·98
80	1,280	3·11	1,145	3·06
81	1,350	3·13	1,250	3·10
82	1,420	3·15	—	—
84	1,540	3·19	1,320	3·12

TABLE V.

$(Am_2O)_37MoO_3$. *Formation Period* 1 *Day.*

Temp. ° C.	50 Volts.	
	Microamps / Sq. Cm.	$Log_{10}i$.
15	13·8	1·14
20	20·2	1·33
25	28·2	1·45
30	42·2	1·62
35	57	1·76
40	84·5	1·93
45	114	2·06
50	149	2·17
55	—	—
60	292	2·46
62·5	362	2·56
65	403	2·60
67·5	455	2·66
70	550	2·74
72·5	660	2·82
75	743	2·88
77·5	950	2·98
80	1,110	3·05

TABLE VI.

$Am_2C_2O_4$. *Formation Period* 1 *Day.*

Temp. ° C.	50 Volts.		25 Volts.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
15	86	1·93	74·2	1·87
20	118	2·07	110	2·04
25	165	2·22	152	2·18
30	233	2·37	211	2·32
35	340	2·53	304	2·48
40	495	2·69	435	2·64
45	710	2·85	—	—
50	947	2·97	826	2·92
55	1,250	3·10	1,120	3·05
60	1,720	3·24	1,490	3·17
62·5	2,160	3·34	1,930	3·29
65	2,340	3·37	2,110	3·32
67·5	3,030	3·48	2,420	3·39
70	3,270	3·56	3,010	3·48
72·5	3,960	3·60	—	—
75	4,900	3·69	4,010	3·60
77·5	5,700	3·76	4,400	3·69
80	—	—	5,600	3·75

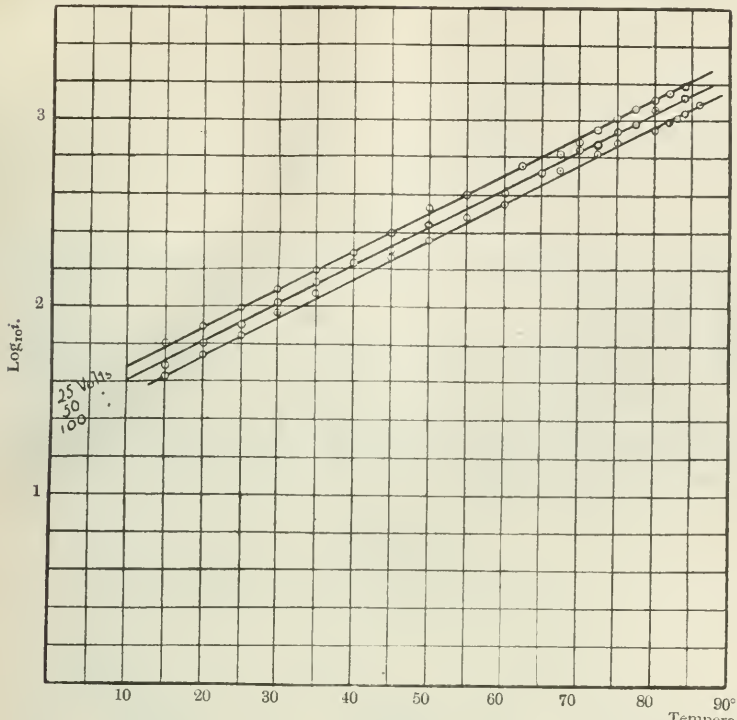


FIG. 5.—Am_2HPO_4, 1 Day's Formation at various Voltages.

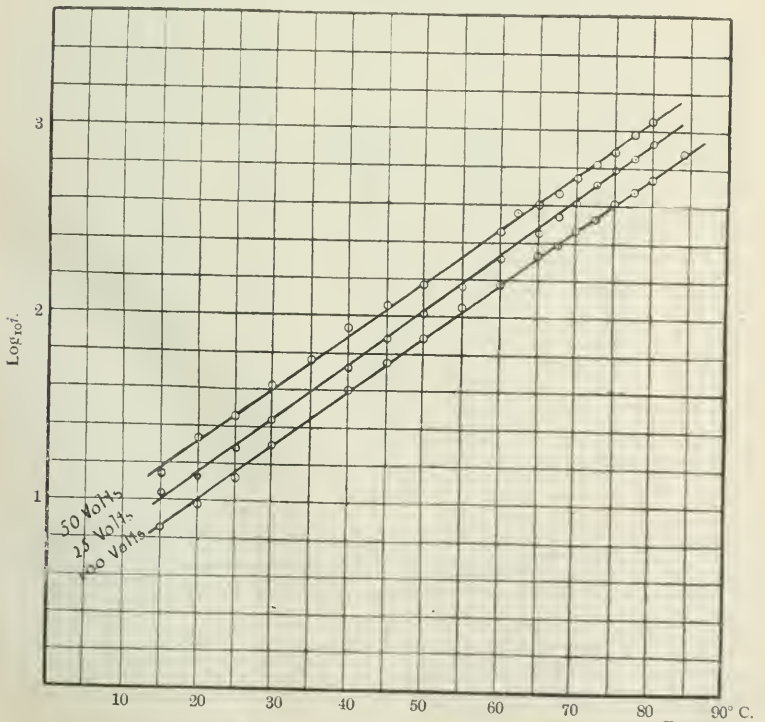


FIG. 6.—$(Am_2O)_37(MoO_3)$, 1 Day's Formation at various Voltages.

Voltage.	*a*.
25	·0990
50	·0952
100	·0930

It will be noticed that the line representing the second stage is less steep for 100 volts than it is for 50 or 25, and leaves the line belonging to the first stage more abruptly.

The above facts may be explained in the following manner. A solution of $AmHCO_3$ at a temperature of 58° (which is near the turning-point above mentioned, 55°) decomposes into carbon dioxide and ammonia, and we may assume therefore that at about this temperature the basic carbonate forming the film on the anode will change its composition and become practically the oxide, so that the first part of the curves refers to a film of the basic

TABLE VII.

$AmHCO_3$. *Formation Period* 1 *Day.*

Temp. ° C.	25 Volts.		50 Volts.		100 Volts.	
	Microamps / Sq. Cm.	$\text{Log}_{10}i$.	Microamps / Sq. Cm.	$\text{Log}_{10}i$.	Microamps / Sq. Cm.	$\text{Log}_{10}i$.
15	5·6	·75	8·2	·91	11·4	1·06
20	6·7	·84	10·9	1·04	16·6	1·22
25	11·0	1·04	16·0	1·20	22·2	1·35
30	17·2	1·24	21·9	1·34	31·7	1·50
35	22·0	1·34	31·8	1·50	46	1·66
40	31·6	1·49	48·2	1·68	70	1·84
45	49	1·69	71	1·85	96	1·96
50	72·5	1·86	100	2·00	143	2·15
55	110	2·04	137	2·14	160	2·20
57·5	—	—	—	—	203	2·31
60	135	2·13	179	2·25	212	2·33
62·5	148	2·17	194	2·28	228	2·36
65	169	2·23	197	2·29	237	2·38
67·5	184	2·27	213	2·33	265	2·42
70	207	2·32	235	2·37	—	—
72·5	231	2·35	286	2·46	302	2·48
75	277	2·44	344	2·53	329	2·52
77·5	291	2·46	350	2·55	380	2·58
80	338	2·53	360	2·56	400	2·60

carbonate and the second to one of the oxide. We may imagine the film to be more stable at a low voltage than at a high one, so that the initial line will be steeper at a lower voltage, and further, the final line also to be steeper at a lower voltage.

If now we were to test an anode formed in a solution of ammonia, we should expect the line representing the variation of the logarithm of its leakage current with temperature to be straight throughout its course and

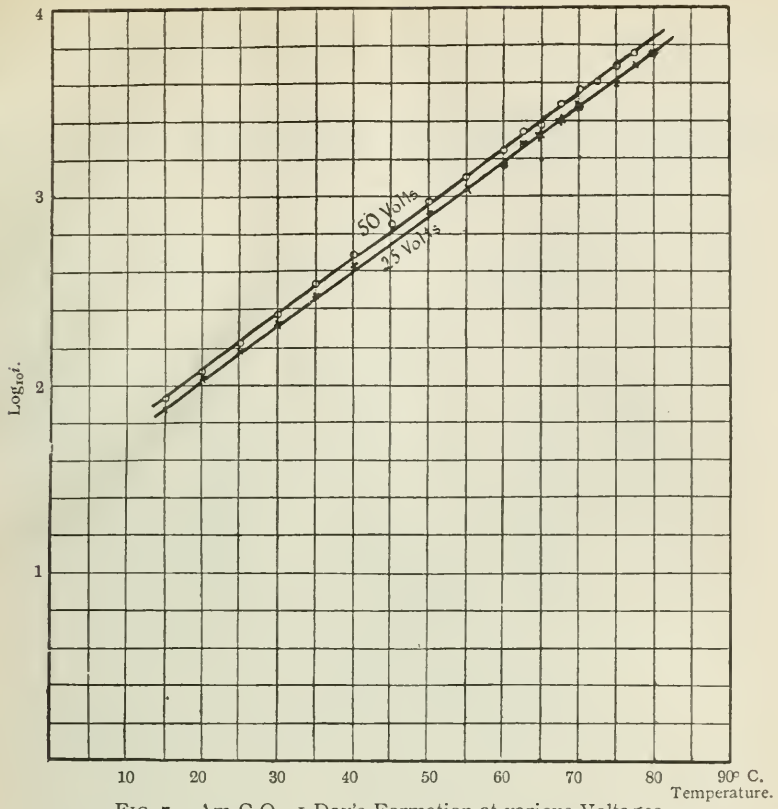


FIG. 7.—$Am_2C_2O_4$, 1 Day's Formation at various Voltages.

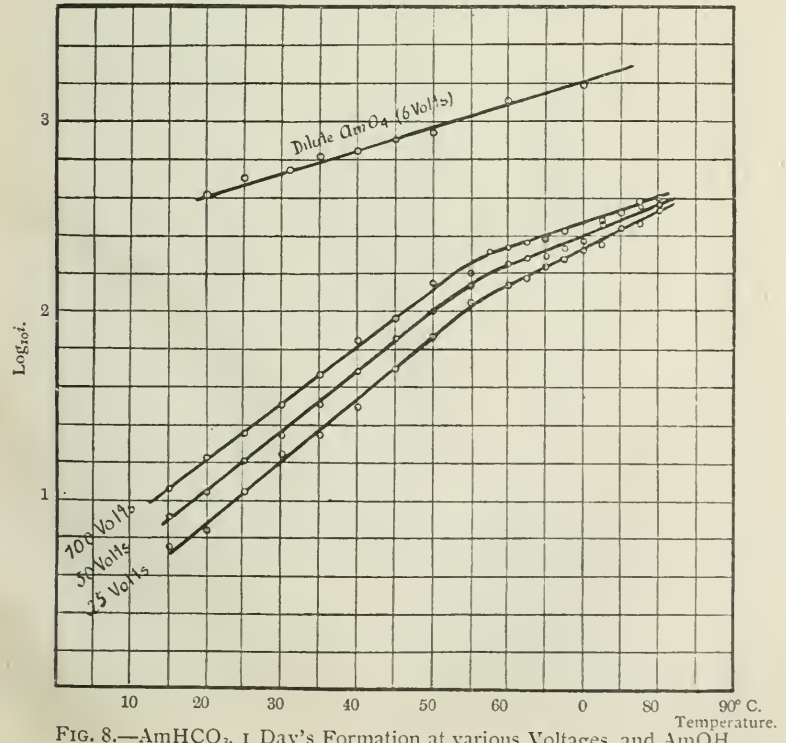


FIG. 8.—$AmHCO_3$, 1 Day's Formation at various Voltages, and AmOH (dilute) at 6 Volts.

to be parallel with, or perhaps not quite so steep as, the final part of the 100-volt curve. The upper line in the same figure gives the results of such a test made with dilute AmOH at 6 volts after one day's formation. It will be seen

TABLE VIII.

Dilute AmOH. 1 *Day's Formation at* 6 *Volts.*

Temp. ° C.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$.	$\text{Log}_{10} i$.
20	408	2·61
25	500	2·70
31	550	2·74
35	650	2·81
40	690	2·84
45	805	2·90
55	1,090	3·04
60	1,280	3·11
70	1,560	3·19

TABLE IX.

$(Am_2O)_37(MoO_3)$. 1 *Day.* 100 *Volts.*

Temp. ° C.	Concentration = $\frac{1}{2}$ (Saturation).		Concentration = $\frac{1}{8}$ (Saturation).	
	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$.	$\text{Log}_{10} i$.	$\frac{\text{Microamps}}{\text{Sq. Cm.}}$.	$\text{Log}_{10} i$.
15	11·1	1·05	12·9	1·10
20	14·2	1·16	16·3	1·21
25	20·2	1·30	24·7	1·39
30	29·2	1·47	33·7	1·53
35	42·4	1·63	48	1·68
40	59·2	1·77	69	1·84
45	84·5	1·93	96	1·98
50	117	2·07	137	2·14
55	163	2·22	186	2·27
60	218	2·34	249	2·40
62·5	262	2·42	284	2·45
65	305	2·49	336	2·54
67·5	341	2·53	—	—
70	415	2·62	363	2·56
72·5	470	2·67	—	—
75	530	2·73	690	2·84
80	755	2·88	906	2·96
84	—	—	1,110	3·05

that it has the above-mentioned characteristics, its a being ·0335 as against ·0395, the value for the upper part of the 100-volt curve.

The experimental results of the AmOH test are given in Table VIII.

4. *The Influence of the Concentration of the Electrolyte.*

Since the general result of decreasing the concentration of the electrolyte in which an Al anode-film is formed is to increase the leakage current, it

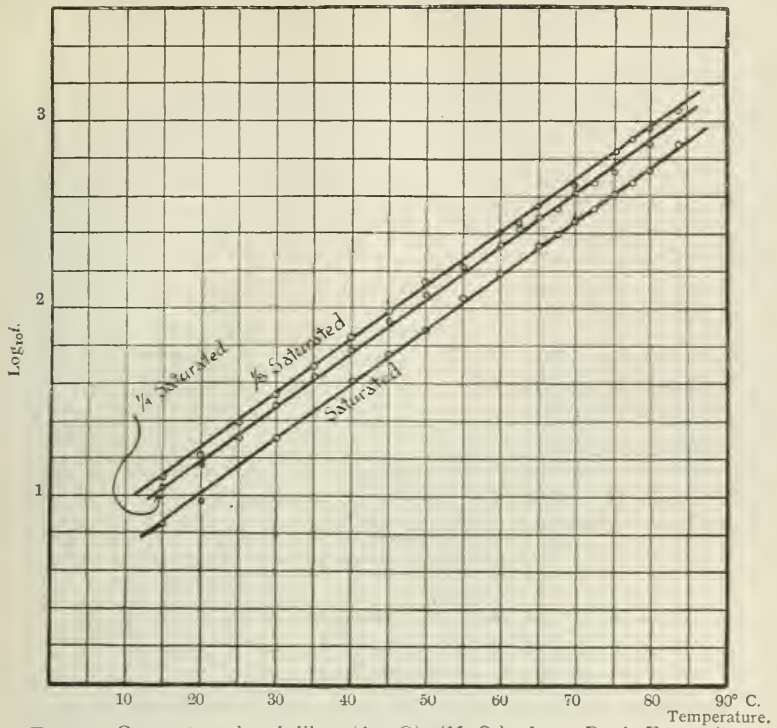


FIG. 9.—Concentrated and dilute $(Am_2O)_37(MoO_3)$ after 1 Day's Formation at 100 Volts.

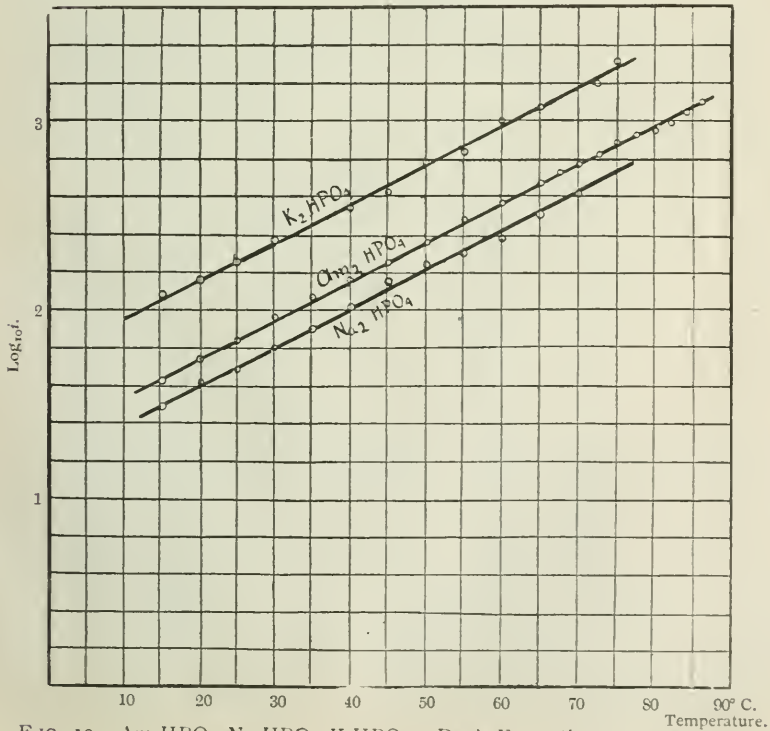


FIG. 10.—Am_2HPO_4, Na_2HPO_4, K_2HPO_4, 1 Day's Formation at 100 Volts.

TABLE X.

1 *Day. Formation Volts* 100.

Temp. ° C.	Na_2HPO_4.		K_2HPO_4.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
15	30	1·48	119	2·08
20	41	1·61	146	2·16
25	48	1·68	179	2·25
30	63	1·80	236	2·37
35	79	1·90	—	—
40	104	2·02	345	2·54
45	141	2·15	415	2·62
50	174	2·24	600	2·78
55	200	2·30	695	2·84
60	239	2·38	1,010	3·00
65	334	2·52	1,180	3·07
70	413	2·62	1,470	3·17
72·5	—	—	1,580	3·20
75	—	—	2,060	3·31

TABLE XI.

$(Am_2O)_37(MoO_3)$. *Formation Volts* 100. *Tested at various Voltages.*

Temp. °C.	90 Volts.		75 Volts.		50 Volts.		25 Volts.	
	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.	Microamps / Sq. Cm.	$Log_{10}i$.
20	4·15	·62	2·10	·33	1·28	·11	·63	$\bar{1}$·80
25	5·76	·76	—	—	1·80	·25	·91	$\bar{1}$·96
30	8·2	·91	4·2	·62	2·45	·39	1·16	·06
35	10·5	1·02	4·45	·65	3·25	·51	1·43	·16
40	—	—	7·05	·88	4·55	·66	1·89	·28
45	22·3	1·35	9·35	·97	6·3	·80	2·65	·42
50	27·7	1·44	14·8	1·17	8·6	·93	3·38	·53
55	50·1	1·70	18·3	1·26	12·4	1·09	4·45	·65
60	95	1·98	24·5	1·37	14·8	1·17	5·84	·77
62	133	2·12	28·7	1·40	17·0	1·23	7·22	·86
64	182	2·26	33·8 (65°)	1·53	21·5 (65°)	1·33	8·00 (65°)	·90
66	252	2·40	—	—	—	—	—	—
68	275	2·44	43·8 (67·5°)	1·64	23·3 (67·5°)	1·37	9·4 (67·5°)	·97
70	330	2·52	57·2	1·76	29·5	1·47	10·8	1·03
72	392	2·59	116	2·05	—	—	—	—
74	442	2·65	288	2·46	50·5	1·71	14·6	1·16
76	501	2·70	535	2·73	79	1·90	17·5	1·24
78	627	2·80	—	—	112	2·05	24·2	1·38
80	750	2·87	822	2·91	185	2·21	35·5	2·55
81	791	2·90	872	2·94	254	2·40	44·6	1·65
82	—	—	—	—	345	2·54	60	1·78
83	—	—	—	—	477	2·68	83	1·92
84	—	—	—	—	670	2·83	133	2·12
85	—	—	—	—	1,220	3·09	191	2·28
86	—	—	—	—	—	—	890	2·95

might be supposed that a film formed in a weak solution would not give the same value for *a* as one formed in a strong solution. However, this is not the case, as Table IX. and Fig. 9 show. Here curves are given for a concentrated solution of $(Am_2O)_37(MoO_3)$ for one day's formation at 100 volts, and also for very weak solutions of one-quarter and one-eighth of that of a concentrated solution respectively, and again we have a set of parallel straight lines, the values of *a* being ·0870, ·0872, and ·0865 respectively.

5. *A Comparison of the Behaviour of a Series of Electrolytes having the same Anion.*

The previous work has shown that the only variable so far considered that has any influence on *a* is the nature of the electrolyte. The question presents itself as to whether the cation has any influence on the value of *a*. Table X. and Fig. 10 illustrate this point. They give the results for the three phosphates of ammonium, sodium, and potassium. It will be seen that while the initial value of A varies considerably with the nature of the cation, *a* has the value ·0612, ·0615, and ·0610 respectively for the three phosphates, and is therefore independent of the cation.

6. The Influence of the Voltage at which the Test is made.

The final variable whose influence has to be considered is that of the voltage used during the test. Table XI. gives the results for films formed at 100 volts in $(Am_2O)_37(MoO_3)$ for one day, with the temperature tests made at 90, 75, 50, and 25 volts respectively.

In Fig. 11 we have the usual log *i* curves plotted to temperature. It will be seen that each curve is straight for part of its course, but that at a certain point it curves up, crosses the normal curve for a test made at the voltage of formation, and finally tends to become parallel to it. The lower the voltage the more rapidly does it curve up. The straight portions of the lines are not quite parallel to one another ; as the voltage decreases the gradient becomes gradually smaller, as the following table shows :—

Voltage of Test.	*a*.
100	·0875
90	·0840
75	·0810
50	·0710
25	·0655

Another point of interest is that all the curves depart from a straight line at practically the same current density ; this is shown by the dotted line, which corresponds to a current density of about 200 microamps per square centimetre.

In Figs. 12 and 13 the variation of the current density with the voltage of the film formed at 100 volts is delineated for different temperatures. In Fig. 12 the results are given for steps of temperature of 10° from 20° to 60°. It will be seen that for most of the range of voltage they are straight, but rapidly shoot up as the voltage of formation is reached, and that as the temperature rises the part of the curve which is straight becomes shorter and shorter. Above 60° the shape of the curves alters (in Fig. 13 they have been

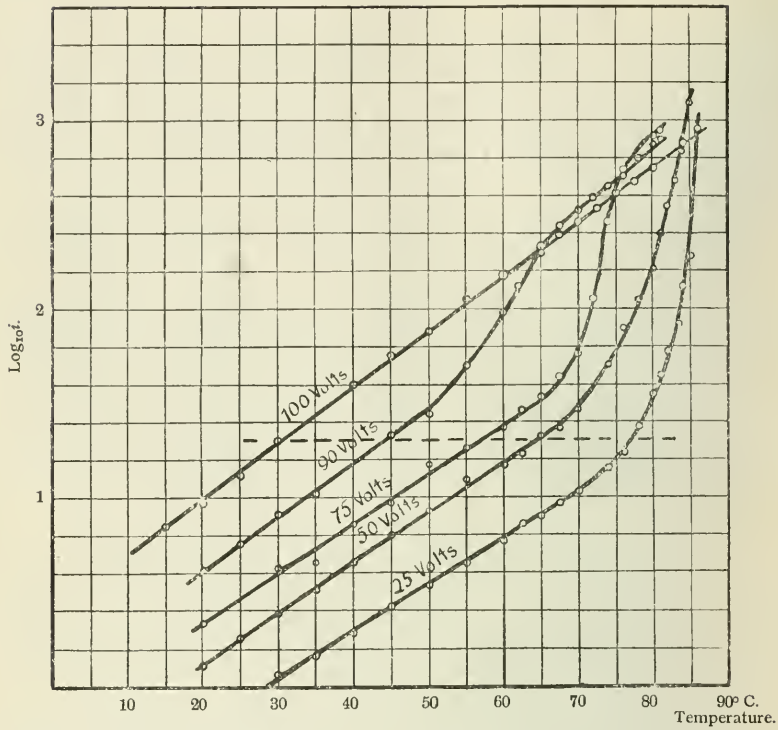


FIG. 11.—$(Am_2O)_37(MoO_3)$ formed at 100 Volts and tested at various Voltages.

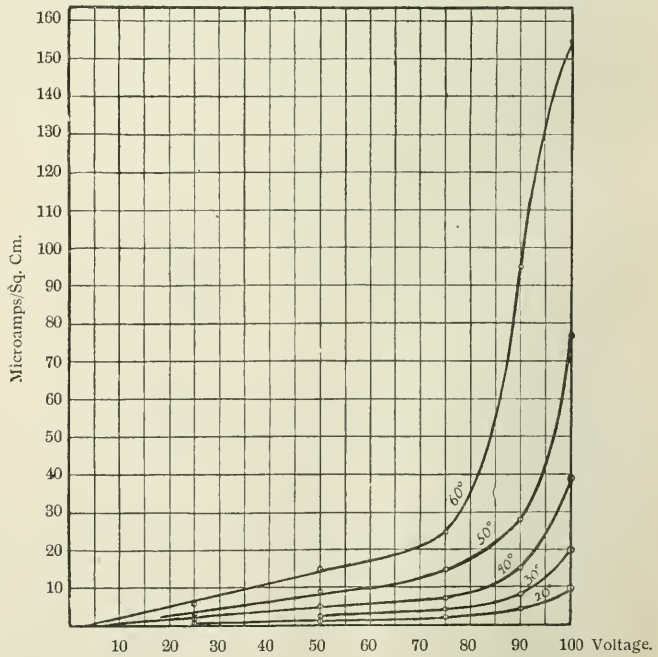


FIG. 12.—Showing the Variation of Current Density with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures (low).

TABLE XII.

Cooling-down Experiments. $(Am_2O)_37(MoO_3)$. 1 *Day's Formation.*

Temp. °C.	25 Volts.				50 Volts.			
	Ascending Temp.		Descending Temp.		Ascending Temp.		Descending Temp.	
	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.
20	13·2	1·12	—	—	20·2	1·33	—	—
25	18·6	1·27	28·2	1·45	28·2	1·45	—	—
30	26·8	1·43	36·4	1·56	42·2	1·62	—	—
35	—	—	49	1·69	57	1·76	94	1·97
40	52	1·72	80	1·90	84·5	1·93	112	2·05
45	76	1·88	114	2·06	114	2·06	162	2·21
50	102	2·01	135	2·12	149	2·17	—	—
55	144	2·16	197	2·27	—	—	302	2·48
60	202	2·31	268	2·43	292	2·46	427	2·63
62·5	—	—	—	—	362	2·56	—	—
65	285	2·45	345	2·54	403	2·60	555	2·74
67·5	348	2·54	—	—	455	2·66	—	—
70	417	2·61	520	2·72	550	2·74	780	2·89
72·5	510	2·71	—	—	660	2·82	—	—
75	615	2·79	675	2·83	745	2·88	1010	3·00
77·5	745	2·87	—	—	950	2·98	—	—
80	850	2·93	—	—	1,110	3·05	—	—

TABLE XIII.

Cooling-down Experiments. $Am_2B_4O_7$. 1 *Day's Formation.*

Temp. °C.	25 Volts.				100 Volts.			
	Ascending Temp.		Descending Temp.		Ascending Temp.		Descending Temp.	
	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.	Microamps. / Sq. Cm.	$Log_{10}i$.
20	2·4	1·38	—	—	4·3	·63	—	—
25	3·6	1·56	6·9	·84	6·65	·82	2·15	·32
30	5·4	1·73	10·9	1·04	10·8	1·03	—	—
35	—	—	16·7	1·22	21	1·30	48·7	1·69
40	16·8	1·23	31	1·49	30·7	1·49	74	1·87
45	25·5	1·41	51	1·71	50·2	1·70	108	2·03
50	49	1·69	95	1·98	94	1·97	—	—
55	79	1·90	164	2·22	147	2·17	284	2·45
60	154	2·19	224	2·35	233	2·37	468	2·67
62·5	168	2·23	—	—	306	2·49	—	—
65	237	2·37	400	2·60	416	2·62	—	—
67·5	296	2·47	—	—	562	2·75	800	2·90
70	390	2·59	695	2·84	780	2·89	—	—
72·5	502	2·71	—	—	845	2·93	1,120	3·05
75	650	2·81	960	2·98	1,260	3·10	1,340	3·13
77·5	860	2·93	—	—	1,560	3·19	—	—
80	1,140	3·06	—	—	1,910	3·28	—	—
83	—	—	—	—	2,470	3·39	—	—

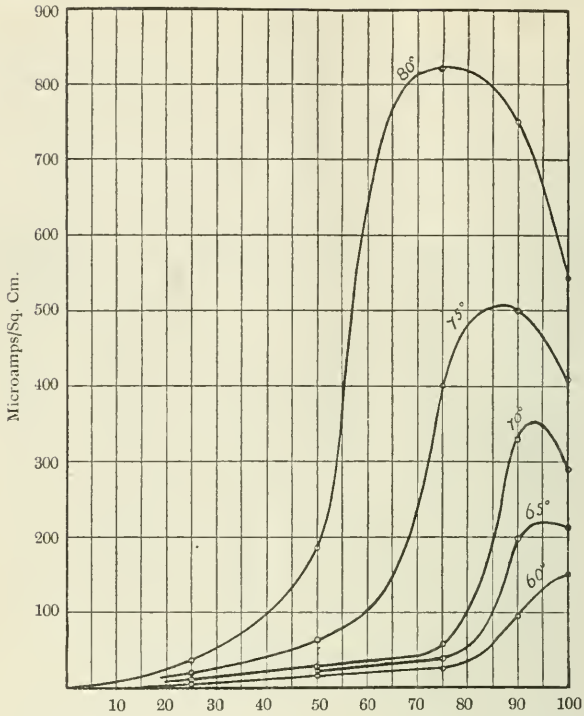


FIG. 13.—Showing the Variation of Current Density with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures (high).

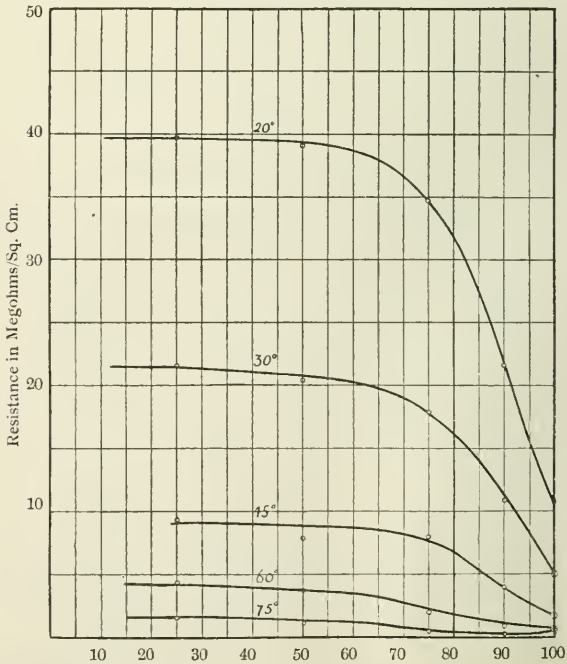


FIG. 14.—Showing the Variation of Resistance with Voltage of an Al Anode-film formed at 100 Volts, for different Temperatures.

plotted for steps of 5° from 60° to 80°) and each tends to reach a maximum, which maximum becomes more and more pronounced as the temperature rises, and occurs at a lower and lower temperature.

In Fig. 14 the results are depicted in a different manner, the resistance being plotted to voltage for different temperatures. Up to about one-half of the voltage of formation, the resistance is practically constant, but rapidly falls off as the voltage reaches that of formation.

7. *The Connection of "a" with the Equivalent Weight of the Anion.*

Since a is a property solely of the anion, the question arises whether there is any numerical relationship existing between them. A brief inspection of Fig. 4 shows that a is not related to the valency of the acid radical. If, however, we calculate the quantity given by the sum of the atomic weights of the elements in the anion and divide this by the valency, *i.e.*, the equivalent weight of the anion, it will be found that one is a definite function of the other, as the following table shows :—

Anion.	Equivalent Weight.	a.
B_4O_7''	78	·1090
HCO_3'	61	·0990
MoO_3'''	48	·0890
C_2O_4''	44	·0865
PO_4'''	31	·0612
OH'	17	·0335

a increases with the equivalent weight, and if one is plotted against the other (see Fig. 15) they give a very good curve—a curve which is a straight line initially and then gradually bends over.

In the above table the value taken for the HCO_3 anion is that corresponding to the 25-volt curve, since it has been shown this is a truer figure than that for a higher voltage, because of the influence of the OH anion.

When once this curve has been obtained it furnishes us with a method for the determination of the equivalent weight of the anion in an electrolyte.

8. *Cooling-down Curves.*

The final question to be considered is whether, after the electrolyte has been carried up to the boiling-point, the conductivity for decreasing temperatures is the same as for increasing temperatures. This point is illustrated by Table XII. and Fig. 16, which give the heating-up and cooling-down curves for $(Am_2O)_37(MoO_3)$, for 25 and 50 volts. In each case the cooling-down curve is higher, but eventually as the temperature falls, becomes nearly parallel to the heating-up curve. There is perhaps a tendency for a to be slightly less. This becomes more marked in the 100-volt curve for $Am_2B_4O_7$ given in the next figure (see Table XIII. and Fig. 17).

Summary.

1. The law of the variation of the conductivity of an Al anode-film with temperature is given by $i = Ae^{a\theta}$, the curves obtained by plotting log. i to θ being straight lines over the whole range of temperature from ordinary temperatures to the boiling-point of the electrolyte.

2. The value of the exponent a is independent of the voltage of formation, the time of formation, the concentration of the electrolyte, and the cation present in the electrolyte, and depends only on the anion (provided the test

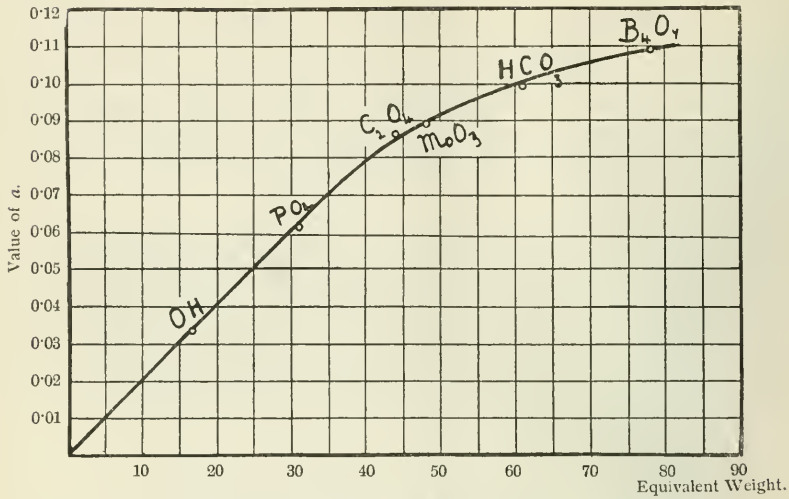


FIG. 15.—Showing the Variation of a with the Equivalent Weight of the Anion present in the Electrolyte.

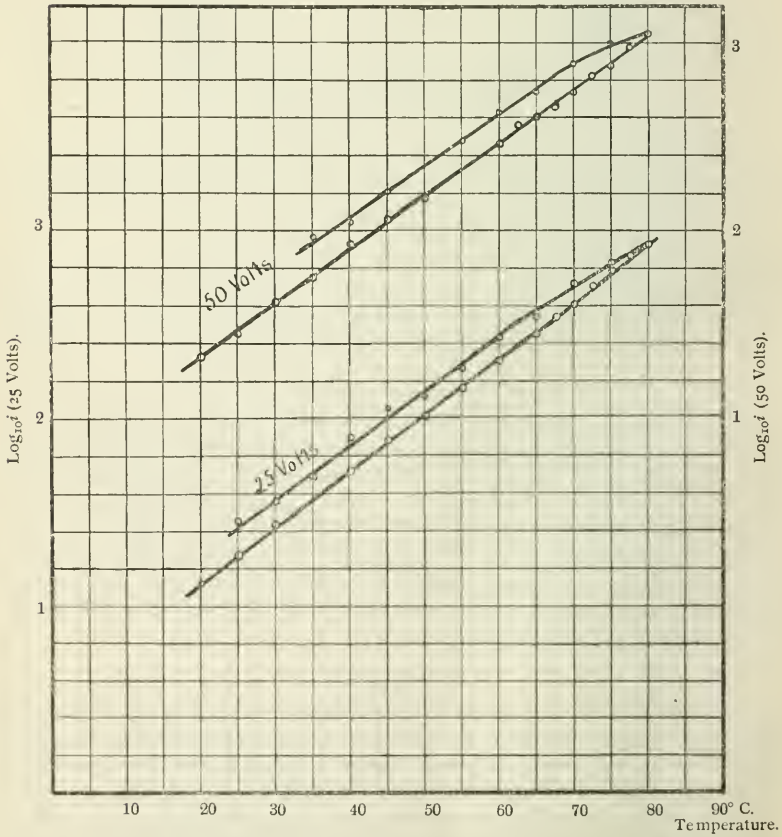


FIG. 16.—Heating-up and Cooling-down Curves for $(Am_2O)_37(MoO_3)$.
(The lower portion of each curve refers to rising temperatures, the upper to falling temperatures.)

is made at the voltage of formation), whereas A varies widely with these variables.

3. $AmHCO_3$ is an exception to the general law. At 55° its a abruptly changes, but this behaviour is explained by the decomposition of the film and by the OH ions playing most part in the conduction.

4. For a given formation voltage a decreases with the voltage of test, but when a certain current density (which is the same for all voltages of test) is reached, the conductivity increases much more rapidly than that given by $A\epsilon^{a\theta}$, in such a fashion that for temperatures above about 60° the current-volt curves have a maximum at a voltage below that of formation.

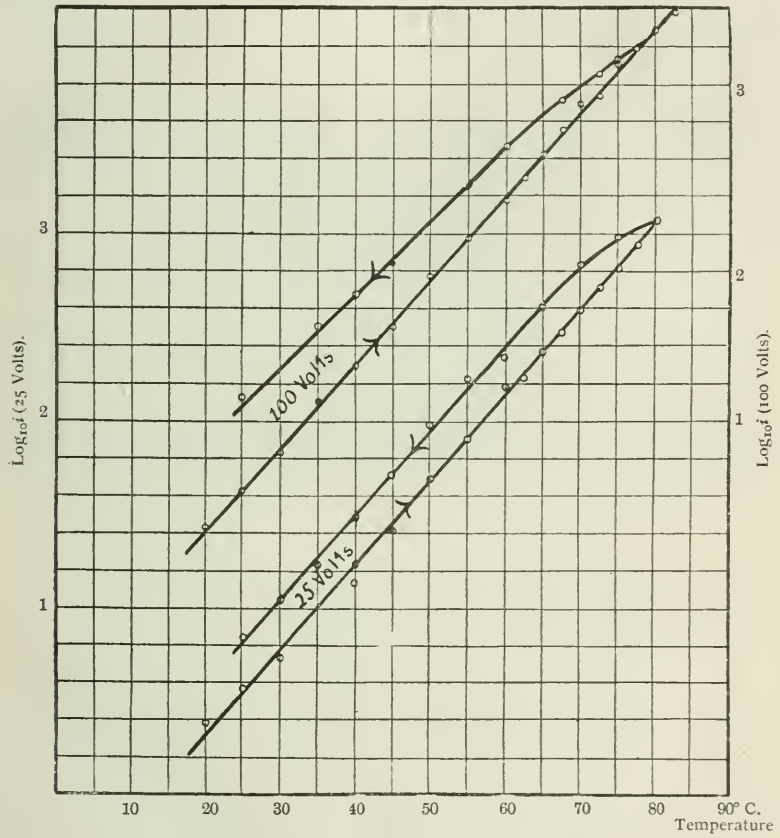


FIG. 17.—Heating-up and Cooling-down Curves for $Am_2B_4O_7$.

5. For voltages up to about one-half of the voltage of formation the resistance of an Al anode-film is practically constant, but rapidly falls off as the voltage reaches that of formation.

6. a is a definite function of the equivalent weight of the anion in solution, and it furnishes a means of determining the latter quantity.

7. A cooling-down curve lies above the heating-up curve, but a ultimately becomes practically the same for both.

The above experiments were carried out in the Laboratories of Applied Electricity, Liverpool University.

May, 1911.

DISCUSSION.

Mr. Robert G. Lunnon said he would like to know how the theory regarding the dual nature of the films which Mr. Bairsto put forward in his previous Paper would explain the exponential temperature law.

Dr. W. C. McC. Lewis asked why the general results of decreasing the concentration of the electrolyte in which a film is formed was to increase the leakage current. Dr. Lewis said he would have thought it was the other way about.

Mr. G. E. Bairsto (*communicated reply*): In reply to Mr. Lunnon's question, although we have a certain amount of knowledge regarding the statics of these films, we have no data on which to work out the dynamical aspect of the question, *i.e.*, to calculate the current required to maintain an anode film in a given condition.

Looking at it from quite a physical point of view, I have tried to find an expression for the current through the film on the assumption that we have a discharge of electrons across a very thin stratum (whose thickness is comparable with the dimensions of a molecule), due to a very large potential gradient of the order of 10^6 volts per cm. The temperature variation of this expression is, however, at variance with the experimental results.

Dr. Lewis thinks that a decrease in the concentration of the electrolyte should lead to a decrease of leakage current, and not to an increase. The statement given on page 242 is the general law, provided the voltage of formation is not close to the critical voltage, because in that case, a decrease of concentration means an increase of critical, and therefore quite possibly we might get a decrease in the leakage current.

If we consider that a film formed in water or AmOH has a very much greater leakage current than one formed in a good electrolyte, it must follow that the leakage current will increase with decrease of concentration.

REVIEWS OF BOOKS.

The Energy System of Matter. A Deduction from Terrestrial Energy Phenomena. By JAMES WEIR. (London, 1912 : Longmans, Green and Co., 39, Paternoster Row, E.C. Pp. 200.)

From a consideration of energy relationships the author comes to the extraordinary conclusion that the earth is an isolated mass in space. No energy is transmitted from the sun to the earth, the source of all terrestrial energy being the earth's axial motion. The author appears to consider that the fundamental objection to accepted views is that they involve the existence of an ethereal medium, "of whose existence there is absolutely no evidential proof." A writer who ignores the overwhelming weight of evidence derived from optical and electromagnetic considerations can hardly be expected to be taken very seriously by physicists. The very heat which the sun's rays pour daily on the earth is said by the author to be derived from its energy of rotation, the influence of the sun's "thermal field" being merely "inceptive," as he styles it. No evidence is offered in support of this so-called theory of inception, and why it should be more scientific to imagine such an inexplicable and incomprehensible process than it is to conceive of an ether (not that transmission of energy from the sun to the earth is necessarily ethereal) the writer has not been able to discover, and least of all from any arguments put forward in this book by Mr. Weir.

Magnetism and Electricity. A Manual for Students in Advanced Classes. By E. E. BROOKS, B.Sc., A.M.I.E.E., and A. W. POYSER, M.A. (London, 1912 : Longmans, Green and Co., 39, Paternoster Row, E.C. Pp. 633, 413 illustrations. Price 7s. 6d. net.)

This is a comprehensive and indeed a very excellent text-book of magnetism and electricity, but with all deference to the authors' teaching experience, we are inclined to think that if more space had been devoted to the exposition of general principles and less to the description of detailed applications, the book would have been even more suitable than it is "for the majority of students before they begin to specialise either in pure science or in the various branches of electrical engineering." Be that as it may, the authors have nevertheless succeeded in making their subject a very real and living one, and to whatever branch of electricity the student will turn, from atmospheric electricity or discharge through gases to electric lamps, or wireless telegraphy, he will find reference to the most recent knowledge and to the latest applications. The book is written on orthodox lines, beginning with electrostatics, and passing on to magnetism, voltaic electricity, and electromagnetism. The illustrations are numerous and good, the majority—unusual in text-books—having been specially drawn for the purpose, while in every chapter numerical examples will keep the student in close touch with concrete and measurable realities.

Elementary Chemical Theory and Calculations. By Joseph Knox, D.Sc. (London, 1912: Gurney and Jackson, 33, Paternoster Row, E.C. Pp. 100. Price 2s. net.)

This useful little book contains concise statements of the chief laws of chemistry and numerical exercises to illustrate all the different calculations met with in an elementary course of chemistry. The work has been thoroughly done, and leaves little room for anything but commendation.

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S., assisted by eminent contributors. Revised and Enlarged Edition, in Five Volumes. Vol. I., pp. 758, A—Che. Vol. II., pp 786, Chi—Go. (London, 1912: Longmans, Green & Co., 39, Paternoster Row, E.C. Price 45s. net per volume.)

It is now more than twenty years since the first edition of Thorpe's famous Dictionary made its appearance, and the magnitude and importance of recent developments in technical chemistry have made the publication of a second edition imperative if it was to retain its honoured position as *the* book of reference *par excellence* for chemists engaged in the industrial applications of their science. The present edition is of course much more than a mere revision of its predecessor, since in addition to the large number of important new articles to be found here, many of the old articles have been entirely re-written and all have been thoroughly revised and brought up to date. It would be impossible here to give anything approaching an adequate account of the contents of a work of reference of such a magnitude; to mention any one of its innumerable excellent articles would be invidious: we can only say that where we have tested it we have found the information it gives to be at once reliable and comprehensive within the limits of possibility, while its references seem almost invariably to take account of the most recent work in the subject under review. It is a pity, however, that whereas most of the articles contain full references in the text or a bibliography at the end on the literature of the particular subject, in some cases references are very meagre, if not absent entirely. We venture to hope that this defect will be remedied in the volumes which are still to appear. Chemists of all kinds will hail the reappearance of "Thorpe" with gratitude and enthusiasm, and the editor, his collaborators and the publishers are to be warmly congratulated on the consummation of their labours.

A Primer on Alternating Currents. By W. G. Rhodes. (London, 1912: Longmans, Green & Co., 39, Paternoster Row, E.C. Pp. 142. Price 2s. 6d. net.)

This book is intended for those whose mathematical attainments do not extend beyond the elements of algebra, and for a student having this knowledge and a moderate mathematical ability it should form a valuable introduction to alternating-current theory. The subject-matter is limited almost entirely to the theoretical side, details of construction and practice being frankly omitted. A short introductory chapter is devoted to establishing the fundamental trigonometrical theorems, and to a clear establishment of the idea of rate of change of a variable, after which the effects of resistance, inductance and capacity are introduced in an easily assimilated way. The latter part of the book deals with transformers, motors, polyphase currents, and rotary converters.

The ground covered is large for a book issued only as a "Primer," but it is covered well. The style is lucid, and the methods are straightforward.

Although the calculus is not employed, there is a commendable absence of the anti-calculus dodges which so often mar books of this nature. No work, however well written, can overcome the troubles imposed by a non-numerical mind, but for the reader with an average mathematical ability Dr. Rhodes's book may be warmly recommended as a stepping-stone to the more advanced aspects of the subject.

The Chemistry of the Radio-Elements. By FREDERICK SODDY, F.R.S. (Monographs on Inorganic and Physical Chemistry. London, 1912: Longmans, Green and Co., 39, Paternoster Row, E.C. Pp. 92. Price 2s. 6d.)

As indicated by the title, this monograph deals almost exclusively with the chemical side of radioactivity. Seeing that the physical side is of equal (many physicists might be tempted to say of greater) importance, the reader lays the book down with a feeling that he has heard only part of the story. It is not quite satisfying, for example, to be told that the atom of uranium on disintegrating expels two α-particles while the atom of radium expels only one, without being given any clue to the reasoning on which these conclusions are based. The term "not separable" used on page 29 and elsewhere in connection with certain groups of radioactive elements seems to be a gratuitous limitation of chemical progress. A few years ago this term might have been applied with almost equal justice to the rare earth elements. It must, however, be admitted that, within the limits which the author has allowed himself, he has on the whole done his work well. The numerous references given at the end of the volume will be useful to students who wish to specialise in radioactivity; but some mention of the more complete works on the subject by the author himself and by others would have been of advantage to the general reader. There are very few misprints; but a minus sign is lacking in two of the equations on page 12. To anyone wishing a concise summary of the results so far achieved in the study of the radio-elements the book may be cordially recommended.

Jahrbuch der Elektrochemie. Edited by Dr. JULIUS MEYER. Vol. xiv. Part I. (Halle-a-S. 1911: Wilhelm Knapp. Pp. 489.)

The present volume of the Jahrbuch appeared at the end of 1911 at the time of going to press with our review of the previous volume (see these *Trans.*, vol. vii., p. 177). We then pointed out that the editor's promise to produce Part II. of vol. xiii. in June, 1911, had not been fulfilled, and as far as we are aware this part has not even yet made its appearance (October, 1912). The same applies to Part II. of the present volume, which was promised for the beginning of the current year. This delay in the publication of the technical part of the Jahrbuch is most regrettable, and it is questionable whether at this rate the Jahrbuch will ever be brought up to date. We have even now only got to the year 1907, and a work of this sort ought really to make its appearance within six months of the end of the year it reports on. It might, therefore, be advisable to proceed at once with the publication of vol. xviii. for 1911 and to produce the intervening volumes as soon as they are ready, a course which we believe was adopted with the "Jahresbericht." As regards the arrangement of the volume under review, we notice that the section dealing with the Reviews of Books has been relegated to Part II. A section on the Atomic Theory has been included after that dealing with Valency, and then follow the sections on Didactics and Apparatus, which in previous volumes appeared immediately after the Reviews of Books. The section on the Phase Rule has been much enlarged and now bears the title "Heterogene Gleichgewichte."

Then follow Section III. on Homogeneous Equilibria and State in Solution (pp. 122–173), Section IV. on Reaction Velocities and Catalysis (pp. 173–210), Section V. on Thermochemistry (pp. 210–241), Section VI. on Photochemistry (pp. 241–250). It will be seen, therefore, that the general arrangement differs somewhat from that of previous volumes, and is, probably, in its present form preferable. The next three sections—Conductivity (pp. 250–293), Chemical and Electrical Energy (pp. 293–382), Electric Phenomena in Gases (pp. 382–409)—correspond with those of previous volumes. The final Section XIII. (pp. 410–489) deals with Colloids in a masterly and comprehensive fashion. This section in the previous volume came much earlier in the work. A short list of Corrigenda is added, and *apropos* of this, we must admit that in comparison with former volumes of the Jahrbuch, the one under review seems to be singularly free from misprints as regards authors' names. Individual comment in a work of this nature is practically impossible, but a careful perusal has convinced us that little has been omitted and that the abstracts are well done and criticisms fair. But we cannot conclude without once more expressing our regret that only half the Jahrbuch is available. There is, of course, no index to these first parts, and without it the volume as a work of reference is of little value, as it is almost hopeless to find any abstract required without wading through the whole book, and even then it may not be there at all. We hope that editor and publisher will use every effort to complete Vols. XIII. and XIV. as soon as possible, but if there is no hope of this being done at an early date, then, at any rate, to supply at least an index of authors' names to those first parts which have now appeared.

Introduction à l'Étude de la Spectrochimie (Cours professé à la Faculté des Sciences de Paris). By G. URBAIN, Professor de Chimie à la Sorbonne. (Paris, 1911: A. Hermann et Fils. Pp. 245. Price 10 frs.)

This book, in good accordance with its title, deals with the whole of the spectroscopic phenomena likely to be of immediate interest to the chemist, and on the whole with a completeness well proportioned to the importance of each section from the chemical standpoint. It includes sections on emission spectra (flame, Geissler tube, arc, and spark), phosphorescence, absorption. There is further a final chapter dealing with the constitution of spectra which contains certainly as much well condensed matter on this subject as it seems desirable to open up, having in view the purpose of the book, which, in the words of the author, "s'addresse . . . aux jeunes chimistes, qui . . . désireraient acquérir rapidement les notions essentielles, nécessaires pour aborder l'étude théorique et expérimental de la spectrochimie."

Of the above divisions of the subject the one treated at greatest length is that dealing with emission spectra—just that division of the subject the study of which as an aid to chemical analysis was initiated with so much enthusiasm in the days of Kirchhoff and Bunsen, and which, in spite of the enthusiastic advocacy of numerous workers since, has almost entirely failed to develop into a daily instrument of research. M. Urbain's opinion of the value of the spectroscope to the chemist is well illustrated by the following remark: "En analyse chimique, le spectroscope apporte la certitude, là où les méthodes de la chimie pure demeurent impuissantes, ou ne donnent péniblement que de vagues probabilités."

The various reasons which have retarded the growth of spectroscopic methods in the chemical laboratory are extremely well and clearly put forward by the author. That these reasons are not essential in their nature

he clearly shows, and is in no doubt as to the extreme value of the methods he describes. To quote once more: "L'analyse spectrale n'est ni plus capricieuse, ni plus délicate que l'analyse classique. Elle a, comme celle-ci, une technique variée ; et dans la plupart des cas, elle est plus expéditive et plus sure."

This important section of the subject is treated clearly and on the whole with thoroughness. And it is chiefly in the chapter on emission spectra and spectrum analysis that one appreciates the added value which the book derives from the author's approaching his subject as a chemist, for he is able to foresee, and to forewarn the reader concerning, the causes of error which the chemist will encounter in his early essays of spectroscopic methods. It is, however, surprising that in referring to the work of Mons. A. de Gramont on "Les Raies Ultimes" he should have neglected entirely to mention the extremely important and closely allied work of Dr. J. H. Pollok, in which he has carried forward Hartley's researches on the quantitative spectra of metals in solution. Even in the reference to the work of Mons. de Gramont (p. 139), one reference alone, and none of Mons. de Gramont's figures, is given. Since the whole of the more important numerical results of Mons. de Gramont's researches in this direction can be stated in very limited space, it might be suggested that a later edition should make good this omission.

As to absorption, a phenomenon of particular interest to the chemist, as it affords indications of the molecular constitutions of extremely complex bodies, the treatment is scarcely so adequate, one brief chapter of 25 pages being alone allotted to it; and it is unfortunate that just when most observers are recognising the importance of spectrophotometric measurements as alone capable of forming quantitative or even really sound qualitative results (indeed, the author himself remarks on p. 204: "Pour aborder cette étude d'une manière rigoureusement scientifique il faut recourir aux méthodes spectrophotométriques"), he yet dismisses the description of spectrophotometric methods and apparatus in rather less than one page.

A slight error in this section may also be noted which may cause some confusion to the beginner. On p. 205 at the bottom the author says: "Mais on peut à l'aide de ces documents tracer des courbes plus significatives en portant les longueurs d'onde, ou les temps périodiques, en abscisses, et, en ordonnées, non les épaisseurs elles-mêmes mais leurs logarithmes." Actually, of course, one plots as ordinates the logarithms not of the thicknesses but of the absorptions. The advantage derived from this procedure is implied in the generalisation known as Beer's law, which states that in the case of absorbing substances in solution the logarithm of the absorption is proportional to the product—

$$\text{Concentration} \times \text{thickness traversed.}$$

A word of praise should be allotted to the excellent reproductions of spectrum photographs.

One more criticism we should like mildly to offer, namely, that there is no index.

The book may be welcomed as a very valuable introduction to the subject of spectrochemistry.

Physico-chemical Calculations. Joseph Knox. (London, 1912: Methuen & Co., Ltd. Pp. viii + 188. Price 2s. 6d.)

In order to ensure that a student may thoroughly grasp and learn to apply the general principles of Physical Chemistry it is absolutely necessary that he

should solve a series of exercises and problems on the different branches of the subject. As the study of Physical Chemistry is now extending so rapidly, a book devoted exclusively to physico-chemical problems has been needed for some time, and this requirement has now been met in a highly satisfactory way by Dr. Knox. His book is based on the well-known "Rechenaufgaben" of Abegg and Sackur, and is a considerable improvement on the German original.

The book is, of course, meant to be used in conjunction with a text-book of Physical Chemistry. It contains eleven chapters, dealing with the main subdivisions of the subject. Each chapter commences with a brief but clear explanation of the principles and formulæ involved, a number of problems are then worked out in full, and finally a large and well-chosen selection of problems for solution is given. The book is remarkably free from mistakes; in the course of an extended examination the reviewer has noticed only one slight error, in the answer to problem 147. To every student of Physical Chemistry who wishes not merely to understand, but to learn to apply his subject with confidence, Dr. Knox's book is warmly recommended.

A Textbook of Practical Chemistry for Technical Institutes. By A. E. Dunstan, D.Sc., and F. B. Thole, B.Sc. (London, 1912: Methuen & Co., Ltd. Pp. viii + 335. Price 3s. 6d.)

In this book of 335 pages qualitative analysis, gravimetric, volumetric, and gas analysis, common organic operations and physico-chemical measurements are briefly and on the whole adequately described, and the book is remarkably good value for the small cost. The methods are those in general use and call for no special comment. The chapters on volumetric analysis and on the identification of organic compounds are good; that on gravimetric analysis might usefully be made rather longer. Chapter iii., which purports to describe the "reactions of the ions," is perhaps the least satisfactory. The diagrams are poor.

A number of small mistakes should be corrected in a later edition, which should soon be called for. The formula for cuprous chloride is CuCl, not Cu_2Cl_2, and the ferric ion is probably not yellow, as stated on p. 17. The remark on p. 53 about the "perfection" of the periodic law is not very happy, as the periodic classification is far from satisfactory. The frequent use of the term "hydrate" when hydroxide is meant is unfortunate in a modern text-book. These are, however, only slight blemishes in a book which has very considerable merit.

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